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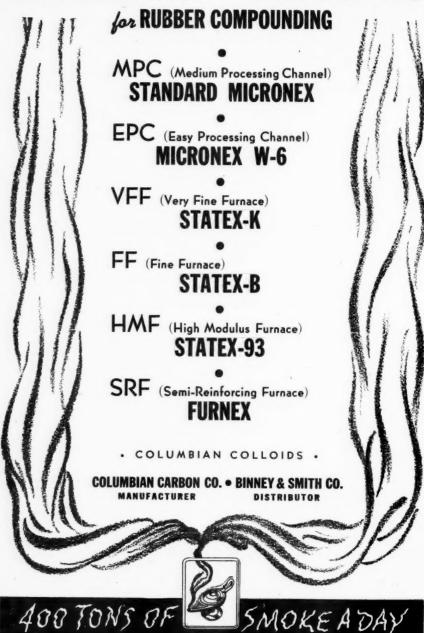
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KINETIC STUDIES IN THE CHEMISTRY OF RUBBER AND RELATED MATERIALS. II. THE KINETICS OF OXIDATION OF UNCONJUGATED OLEFINS *

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The oxidation of olefins generally leads to a complex mixture of products, in which the oxygen may be combined in a number of different ways[1]. Evidence has been accumulated in recent years[2] that, in some cases at least, the major primary product is an unsaturated hydroperoxide, $RCH:CH.CH(O_2H).R'$. Indeed conditions can be found in which certain olefins give a quantitative yield of this material. Under these circumstances we have found it possible to study this particular reaction by kinetic methods, and in this paper are summarized the results so far obtained; full experimental details are in course of publication elsewhere[3].

Most of the work has been carried out on ethyl linoleate I, the other olefins studied being ethyl linolenate II, methyl oleate III, and squalene IV.

(I) $CH_3(CH_2)_4CH{=}CH{-}CH_2{-}CH{=}CH{-}(CH_2)_7COOC_2H_5$

(II) $CH_3.CH_2.CH{=}CH{-}CH_2{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}(CH_2)_7COOC_2H_5$

(III) $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOCH_3$

(IV) $(CH_3)_2C{=}CH.CH_2(CH_2.C(CH_3){=}CH.CH_2)_2(CH_2.CH$
$\qquad\qquad\qquad\qquad {=}C(CH_3)CH_2)_2CH_2.CH{=}C(CH_3)_2$

It will be seen that I is a 1, 4 diolefin; II may be considered as approximately equivalent to two 1, 4 diolefins, III is a monoölefin, while IV contains a repeating 1, 5-diene unit analogous to that present in natural rubber. Rigorous purification was found necessary before reproducible oxidation rates were obtained; this was generally accomplished by a combination of molecular distillation and chromatographic methods.

The peroxide contents of reaction products were determined by two methods: (1) by reaction with ferrous thiocyanate, using a colorimetric estimation of the ferric thiocyanate produced[4]; (2) by the modified iodine method of Dastur and Lea[5]. In general, the results of these methods were in good agreement, but in the case of oxidized ethyl linoleate the former method gave absurdly high values, equivalent to peroxide contents between 1 and 2 times higher than the total oxygen content. The origin of this discrepancy is unknown, and the iodine method has been assumed to give the correct result. Strong confirmation of this assumption is found in the close agreement of this value with (1) the total oxygen content, and (2) the active hydrogen value determined by a modified Zerewitinoff method[6]. Under the experimental conditions employed in the kinetic work, the first three olefins gave quantita-

tive yields of hydroperoxide.   The lower yield found in the case of squalene (see below) makes conclusions drawn from work on this olefin less certain.

Examination of the absorption spectra in the quartz U.V. region has shown[7] that oxidation of the linoleate and linolenate is accompanied by double bond displacement and the formation of conjugated materials.   This displacement is confined to oxidized molecules, and it appears that the principal oxidation product of ethyl linoleate is a conjugated hydroperoxide, *e.g.*, V:

(V) $CH_3(CH_2)_4 . CH(OOH) . CH=CH . CH=CH . (CH_2)_7 . COOC_2H_5$

Kinetic measurements were carried out on samples of about 0.2 gram in small bulbs, which were shaken sufficiently vigorously for the rate of oxidation to be independent of the rate of shaking.   Oxygen uptake was measured by means of a thermostatted constant-pressure gas burette, a pressure range of
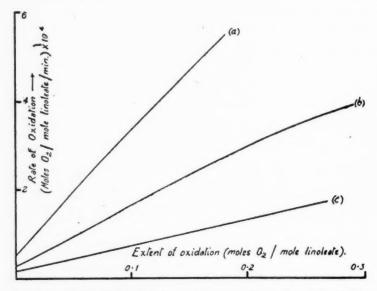
Fig. 1.—Autoxidation of ethyl linoleate at $p_{O_2} = 100$ mm. (a) 55° C; (b) 45° C; (c) 35° C.

5 to 750 mm. being employed.   The reaction vessel was screened from light and separately thermostatted at 25°–75° C.   Carefully purified ethyl stearate was employed as diluent when it was desired to examine the effect of olefin concentration.

THE AUTOXIDATION OF ETHYL LINOLEATE

When pure ethyl linoleate was oxidized, the rate of reaction was found to be small initially and to increase linearly with the extent of oxidation as shown in the typical curves of Figure 1.   Neither the initial rate nor its dependence on extent of oxidation was significantly affected by (1) packing the pyrex reaction vessel with broken glass; (2) coating it completely with polythene, or (3) replacing it by a silica vessel.   It appears, therefore, that the overall oxidation is made up of two homogeneous reactions, of which the first depends only

on olefin and oxygen, and the second involves catalysis by an oxidation product, which must almost certainly be the hydroperoxide. Except in the very early stages, only the catalytic oxidation is of importance, and we consider this first.

Systematic variation of the reactant concentrations showed that over a very wide range the rate of oxidation was represented by an equation of the form:

$$-\frac{d[O_2]}{dt} = k_a[RH][RO_2H]\phi(p) \tag{1}$$

where RH is written for the unoxidized olefin and RO_2H for the hydroperoxide. The form of the pressure variation, $\phi(p)$, was less certainly established, owing to the fact that oxygen pressure had scarcely any effect on the rate until pressures of less than 50 mm. were employed. The measured rates were consistent with the relationship:

$$\frac{1}{\phi(p)} = 1 + \lambda \frac{[RH]}{p} \tag{2}$$

THE MECHANISM OF THE PEROXIDE CATALYZED OXIDATION

By analogy with other autoxidations[8] it was anticipated that this reaction would prove to be of chain character, and this has been shown to be the case by examination of the effects of inhibitors[9]. It is known that benzoyl peroxide readily decomposes thermally, producing free radical fragments which are able to initiate chain reactions[10]. A similar mechanism seemed likely to be responsible for the catalytic activity of the linoleate hydroperoxide, and confirmation of this view has been obtained in two ways: (1) by carrying out a parallel series of oxidations with benzoyl peroxide as catalyst (see below), and (2) by finding experimentally a correlation between the rate of autoxidation and the rate of decomposition of the hydroperoxide. The thermal decomposition of ethyl linoleate hydroperoxide has not yet been fully examined, but it has been shown that the reaction is of second order, i.e.:

$$-\frac{d[RO_2H]}{dt} = k_1[RO_2H]^2 \tag{3}$$

The energy of activation E_1 calculated from the temperature dependence of k_1 is 26 k.cal.

Strong evidence as to the nature of the reaction chain is found in the observation, already noted, that oxidation of ethyl linoleate is accompanied by double bond displacement. This is readily understood if one of the chain carriers is the free radical:

$$R.CH{=}CH.CH.CH{=}CH.R'$$
$$|$$

since this radical possesses two other resonance hybrid configurations:

$$RCH.CH{=}CH.CH{=}CHR' \quad \text{and} \quad R.CH{=}CH.CH{=}CH.CHR'$$
$$| \qquad\qquad\qquad\qquad\qquad\qquad\qquad |$$

The existence of these three alternative forms gives rise to a large resonance stabilization of this radical[11] and also permits the formation of isomeric

peroxide radicals by attack of oxygen, for example:

$$RCH.CH=CH.CH=CHR' + O_2 \longrightarrow RCH.CH=CH.CH=CHR'$$
$$\underset{|}{} \qquad\qquad\qquad\qquad \underset{\overset{|}{O_2}}{}$$

Reaction of this product with a molecule of unoxidized ester could now give the observed hydroperoxide, with formation of a new free radical:

$$RCH.CH=CH.CH=CHR' + RCH=CH.CH_2.CH=CH.R' \longrightarrow$$
$$\underset{\overset{|}{O_2}}{} \qquad\qquad RCH(O_2H)CH=CH.CH=CHR' + RCH=CH.CH.CH=CHR'$$

This reaction sequence, which is shown in the adjoining paper to be energetically reasonable, may be written formally:

$$R- + O_2 \xrightarrow{k_2} RO_2-$$
$$RO_2- + RH \xrightarrow{k_3} RO_2H + R-$$

The initiation process, on this view, must be the production directly or indirectly of R— or RO$_2$— radicals by the decomposition of hydroperoxide. To conform with the results of the decomposition experiments this reaction must be of second order, with a velocity constant k_1:

$$2RO_2H \xrightarrow{k_1} R- + ?$$

To complete the reaction mechanism, we require to know how the chain carriers are destroyed. Since the overall rate is proportional to $[RO_2H]$ while the rate of initiation depends on $[RO_2H]^2$, it is easily seen that the termination must either involve (1) a hydroperoxide molecule and a free radical or (2) two free radicals. Of these alternatives the second is the one to be anticipated on chemical grounds, and is in fact the only one which is consistent with the results of benzoyl peroxide catalyzed oxidation. There are three possible reactions of this type[12]:

$$2R- \xrightarrow{k_4} R-R$$
$$R- + RO_2- \xrightarrow{k_5} R-O-O-R$$
$$2RO_2- \xrightarrow{k_6} R-O-O-R + O_2$$

A complete kinetic analysis, allowing for all three termination reactions, gives no simple explicit rate equation. If (5) and (6) may be neglected it is readily shown that:

$$-\frac{d[O_2]}{dt} = k_2(k_1/k_4)^{\frac{1}{2}}[RO_2H][O_2] \tag{4}$$

while if (4) and (5) are neglected, the rate equation is:

$$-\frac{d[O_2]}{dt} = k_3(k_1/k_6)^{\frac{1}{2}}[RO_2H][RH] \tag{5}$$

Comparing the experimental Equation (1) with (4) and (5) it will be observed that (1) reduces to (4) if p is small, so $\phi(p) \to p/\lambda[RH]$, and to (5) if

p is large ($\phi(p) \to 1$). The physical significance of this is that the concentration of the radicals R— relative to that of RO$_2$— decreases as the pressure increases, so at high pressures the only termination reaction of any importance is that between two RO$_2$— radicals.

An approximate complete treatment is possible by assuming $k_3^2 \simeq k_4 k_6$ when it may be shown that an equation of the same form as (1) is found, with $k_a = k_3(k_1/k_6)^{\frac{1}{2}}$ and

$$\frac{1}{\phi(p)} = 1 + \frac{k_3}{k_2}\sqrt{\frac{k_4}{k_6}}\frac{[\text{RH}]}{[\text{O}_2]} + \frac{\sqrt{k_1 k_4}}{k_2}\frac{[\text{RO}_2\text{H}]}{[\text{O}_2]} \tag{6}$$

For long chains, it is easily seen that the last term is negligible, so (6) is equivalent to (2). In other words, this reaction scheme leads to a completely satisfactory interpretation of the kinetic data. The chain length of the oxidation chain is given by:

$$\nu = \frac{k_3}{\sqrt{k_1 k_6}}\frac{[\text{RH}]}{[\text{RO}_2\text{H}]}\phi(p) \tag{7}$$

With $[\text{RH}]/[\text{RO}_2\text{H}] = 10$, $\phi(p) = 1$, this gives $\nu \simeq 100$ at 45° C. Values calculated from this equation agree reasonably well with those obtained from the study of the effect of inhibitors[9]. No other sequence of reactions has been found which accounts satisfactorily for all the kinetic and chemical observations, and we therefore feel considerable confidence in employing this analysis to discuss the rates and energies of the elementary reactions.

ENERGIES OF ACTIVATION

From the temperature dependence of the overall velocity constant k_a (at $p \to \infty$) we find an energy of activation $E_a = 17.2$ k.cal., which, according to (5), is equal to $E_3 + \frac{1}{2}(E_1 - E_6)$. We have already noted that E_1, measured directly, is 26 k.cal., so that

$$E_3 - \frac{1}{2}E_6 = 4.2 \text{ k.cal.} \tag{8}$$

Similarly, from the temperature dependence of λ, assuming a negligible heat of solution of oxygen, we find:

$$E_\lambda = E_3 - E_2 + \frac{1}{2}(E_4 - E_6) \simeq 8.7 \text{ k.cal.} \tag{9}$$

Combining (8) and (9):

$$\frac{1}{2}E_4 - E_2 \simeq 4.5 \text{ k.cal.} \tag{10}$$

Since reaction (4) involves two free radicals, E_4 must be small (say < 10), so that, even allowing for a rather large experimental error in E_λ, it is clear that $E_2 \simeq 0$. The chemistry of reaction (6) is less clear, so that we can only conclude from (8) that $E_3 > 4$ k.cal.

THE AUTOXIDATION OF ETHYL LINOLENATE

Much less complete data are available for ethyl linolenate, but they suffice to show that the general course of the reaction is identical with that found for ethyl linoleate. The overall energy of activation for the autocatalyzed reaction is almost identical (17.5 k.cal.), and it appears unlikely that any serious differences between the two systems would be revealed by a more detailed analysis.

OXIDATIONS CATALYZED BY BENZOYL PEROXIDE

The rate of oxidation of all the olefins studied was found to be markedly increased in the presence of benzoyl peroxide. To study the kinetics of this reaction separately, it was necessary to deduct the contributions of the uncatalyzed and autocatalyzed reactions. The latter was readily eliminated by measuring the rate in presence of peroxide as a function of extent of oxidation, and extrapolating back to zero. In the case of methyl oleate, this gave at once the rate of the catalyzed reaction, since the uncatalyzed oxidation was negligibly slow under the conditions employed. The rate of the catalyzed reaction was then found to be proportional to the square root of the concentration of benzoyl peroxide, and almost independent of oxygen pressure down to 10 mm. Determination of the dependence on the concentration of olefin presented a slight difficulty, since the rate of oxidation of the solvent (ethyl stearate) was found to be not quite negligible in dilute solution; the rate was, however, very nearly proportional to the concentration of olefin, so we have:

$$-\frac{d[O_2]}{dt} = k_c[RH][Bz_2O_2]^{\frac{1}{2}}\phi(p) \tag{11}$$
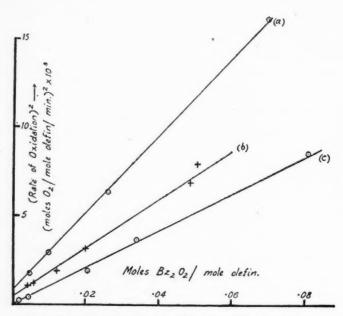
where $\phi(p) \simeq 1$ for methyl oleate.

In the other olefins, the uncatalyzed rate was in general not negligible, and it was necessary to allow for it by means of a linear plot of (rate)^2 against $[Bz_2O_2]$, e.g., in Figure 2. The square root of the slope of this line gave the rate of the catalyzed reaction, which was found to conform closely to Equation (11)[13]. For ethyl linoleate, $\phi(p)$ had the same form as in the autocatalyzed reaction.

Fig. 2.—Benzoyl peroxide-catalyzed oxidation of (a) ethyl linoleate at 45° C; (b) squalene at 45° C; (c) methyl oleate at 65° C. $p_{O_2} = 100$ mm.

It is evident from a comparison of Equations (1) and (11) that the rate equations of the autocatalyzed and benzoyl peroxide catalyzed reactions differ only in the dependence on the content of peroxide. This difference finds a ready interpretation in the observation that the thermal decomposition of benzoyl peroxide is unimolecular, with an energy of activation of 30 k.cal[14]. Strong evidence of the identity of the chain sequences in the autocatalyzed and benzoyl peroxide catalyzed oxidations is found in the close agreement between the rates of oxidation of two samples of ethyl linoleate (1) autocatalyzed, and (2) benzoyl peroxide catalyzed, when the concentrations of the two peroxides were such as to make their decomposition rates equal (at the same temperature).

The overall energies of activation found for the benzoyl peroxide catalyzed oxidation (at $p \rightarrow \infty$) were:

ethyl linoleate	19.0 k.cal.
methyl oleate	23.0 k.cal.
squalene	21.8 k.cal.

The difference between this value for ethyl linoleate and that found for the autocatalyzed reaction should be half the difference between the energies of activation for decomposition of the two peroxides; this is seen to be true within experimental error.

To compare values for the three olefins, we require an expression for the overall rate constant. If k_7 is the unimolecular decomposition constant of benzoyl peroxide, it readily follows that the overall rate constant at high pressures is given by:

$$k_c = k_3 \sqrt{\frac{k_7}{k_6}} \tag{12}$$

The experimentally observed energy E_c is thus $E_3 + \frac{1}{2}(E_7 - E_6)$. Putting $E_7 = 30$ in all cases, we obtain for $E_3 - \frac{1}{2}E_6$ the following values: ethyl linoleate 4 k.cal.; methyl oleate 8 k.cal.; squalene 6.8 k.cal. These are, of course, minimum values for E_3, while the differences between them should represent closely the differences between the absolute E_3 values for the three olefins, since there is no obvious reason to anticipate variations in E_6.

An alternative estimate of the differences in E_3 is obtainable from the relative reaction rates. If we suppose k_6 to be independent of the nature of the olefin, it follows that $k_c \propto k_3$. The only difficulty in applying this method lies in defining [RH] for the three olefins, since this quantity is actually the concentration of readily removable hydrogen atoms. Assuming that the number of reactive methylene groups per molecule is 1 in ethyl linoleate[15], 2 in methyl oleate and 12 in squalene, we find for the relative values of k_3 at 55° C: methyl oleate 1; squalene 2.1; ethyl linoleate 24. If these differences arise solely from differences in E_3, we find:

$$E_3 \text{ (oleate)} - E_3 \text{ (squalene)} = 0.4$$
$$E_3 \text{ (oleate)} - E_3 \text{ (linoleate)} = 2.2$$

The significance of these energy differences will be discussed in the next paper.

NATURE OF THE OXIDATION PRODUCT OF SQUALENE

The above discussion is based on the assumption of a quantitative yield of hydroperoxide, which does not appear to hold in the case of squalene. The

peroxide yield found experimentally was of the order of 40 per cent, and substantially independent of the extent of oxidation in the range 0.7 to 3 per cent oxygen by weight. This figure was confirmed by both methods of peroxide determination, but preliminary active hydrogen estimations suggest a value of the order of one active hydrogen per oxygen molecule introduced. This discrepancy might arise from a decomposition of hydroperoxide during the reaction, but two considerations make this rather unlikely: (1) the failure to find substantially higher peroxide yields at small extents of oxidation, and (2) the observation that the stability of the peroxide on heating in vacuum is of the same order as that of ethyl linoleate hydroperoxide. This difficulty remains to be resolved in the light of further experiment. The close parallelism between the kinetics of benzoyl peroxide-catalyzed oxidation of all the olefins studied makes it appear extremely probable that the essential chain mechanism is formally the same for squalene as for the other olefins.

THE UNCATALYZED OXIDATION OF ETHYL LINOLEATE

Great difficulty was at first experienced in obtaining reproducible values for the initial rate of oxidation, but eventually it was found possible to purify a specimen of the ester by fractional chromatography until further fractionation failed to change the initial rate of oxidation. The main cause of the difficulty is believed to have been traces of free acid, since small additions of stearic acid were found to have a marked catalytic effect, apparently by accelerating the rate of peroxide decomposition. Within the accuracy with which the rather small uncatalyzed rates could be measured, the empirical rate equation was of the form:

$$-\frac{d[O_2]}{dt} = k_u[RH]^{\frac{1}{2}}p^{\frac{1}{2}}\phi(p) \tag{13}$$

where $\phi(p)$ was the same function of oxygen pressure as in the autocatalytic reaction. It is hard to resist the conclusion that we are concerned once more with the same chain sequence, but initiated in this case by

$$RH + O_2 \xrightarrow{k_8} \text{free radicals}$$

(the nature of this reaction is discussed in the following paper). The overall energy of activation for the uncatalyzed reaction is equal to that of the autocatalyzed reaction, within experimental error. It follows that $E_8 \simeq E_1 = 26$ k.cal.

SUMMARY

A brief review is given of kinetic work on the oxidation of representative mono, 1,4 and 1,5 olefins. The essential process in each case is identified as a chain reaction in which hydrocarbon radicals are formed, absorb oxygen, and then react with another molecule of olefin to give a hydroperoxide and a new free radical. Three methods of chain initiation are considered: (1) direct attack of oxygen on the olefin, (2) thermal decomposition of the hydroperoxide, (3) thermal decomposition of added benzoyl peroxide. Chain termination results from interaction of two free radicals; except at low oxygen pressures, these are both peroxidic.

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[12] The nature of the end products is, of course, not determinable by these experiments and may differ from that suggested here. Their concentration is in any case very small if the chain length of the oxidation is long.
[13] It is of interest to note that benzoyl peroxide-catalyzed oxidation of cyclohexene has been studied by Medvedev (*Acta Physico-Chimica U.R.S.S.* **9**, 395 (1938)). His results show the rate of oxidation to be very similar to that of methyl oleate under equivalent conditions. It appears probable from the fragmentary data available that the reaction is also kinetically similar to those we have studied, although Medvedev advances a different interpretation.
[14] McClure, Robertson and Cuthbertson, *Can. J. Research* **20B**, 103 (1942).
[15] Only the most reactive are of course counted; the effect of the less reactive groups flanking the diene system is negligible.

KINETIC STUDIES IN THE CHEMISTRY OF RUBBER AND RELATED MATERIALS. III. THERMO-CHEMISTRY AND MECHANISMS OF OLEFIN OXIDATION *

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In the preceding paper we have considered the kinetics of oxidation of olefins under conditions such that a substantially quantitative yield of hydroperoxide is obtained, and have advanced a mechanism which accords satisfactorily with the experimental data. Part of our purpose in this paper is to show that all the elementary reactions involved in this scheme are thermochemically reasonable. Arising out of this discussion, an attempt is made to define the conditions under which such a reaction sequence will be abandoned in favor of alternatives leading to cyclic or polymeric peroxides, or to hydrocarbon polymers. The chemical evidence[1] suggests strongly that such alternative products are indeed formed in the oxidation of certain olefins, and that they appear to be primary products, and not merely the result of secondary changes of hydroperoxides. That secondary reactions do occur, and are of great importance as oxidation advances, is beyond question, but a consideration of the way in which these take place is outside the scope of the present paper.

The general method of argument followed in this paper is as follows. Suppose we have a series of structurally different olefins, A, B, . . . and that alternative reactions, α, β . . . are possible. For each alternative reaction of each olefin, the heat of reaction may be estimated: suppose these to be $\Delta H_{A\alpha}$, $\Delta H_{A\beta}$, $\Delta H_{B\alpha}$. . . . These heats of reaction may be used in two ways. (1) If the energy of activation E is known from kinetic data, it is clear that we can exclude any mechanism for which $\Delta H > E$. (2) In the absence of any

kinetic evidence, it is not possible to argue that, because $\Delta H_\alpha > \Delta H_\beta$, reaction β will necessarily be preferred to α. If, however, we compare the values of ΔH_α for a series of olefins, there is good reason to expect that the energies of activation for path α lie in the same order as the heats of reaction, so the absolute rates of reaction should be in the reverse order. Similarly the reactivities by path β can be arranged in order. If the actual order of reactivities of the series is known experimentally, comparison with the theory provides evidence as to the actual reaction mechanisms.

The estimation of heats of reaction involves the algebraic summation of the formal strengths of the bonds broken and formed, with corrections for the estimated resonance energies of reactants and products. Except in the final section, we have made no attempt to introduce the effects of hyperconjugation, and we consider in the main only three types of olefin: mono-, 1, 3 di-, and 1, 4-diolefins. To this approximation, double bonds separated by more than one saturated carbon are regarded as isolated. The effects of substituents are only referred to in the last section. The following bond strengths have been employed: C—C, 81 k.cal.[2]; C=C, 145 k.cal.[2]; C—O, 87 k.cal.[3]; C=O, 174 k.cal.[2]; C—H, 99 k.cal.[4]; O=O (oxygen molecule), 118 k.cal.; O—O (peroxide), 66 k.cal.; O—H, 110 k.cal. The only one of these calling for comment is the O—O bond strength in peroxides, for which data in the literature are extremely inconsistent, ranging from 32 k.cal. (from the activation energy of diethyl peroxide decomposition[5]) to approximately 57 k.cal. (from the heats of combustion of ethyl and propyl hydroperoxide and diethyl peroxide[6]). To obtain a more direct estimate of the O—O bond strength in hydroperoxides, the heats of oxidation of ethyl linoleate and linolenate have been measured calorimetrically. The experimental data set out in the next section lead to the figure (66 k.cal.) used in this paper.

THE HEATS OF OXIDATION OF ETHYL
LINOLEATE AND LINOLENATE

The adiabatic calorimeter constructed of pyrex to the design indicated in Figure 1 consisted of a 15 cc. vacuum-jacketed bulb connected through a length of Thiokol tubing to a pumping system and a constant pressure gas burette. Single copper-constantan (32 SWG) thermocouples in series with a Tinsley taut suspension galvanometer (resistance 10 ohms, sensitivity 180 mm. per microamp.) served to indicate any difference in temperature between the contents of the calorimeter and the surrounding water bath. Heat losses along the leads of the resistance heater (about 30 ohms), H, were prevented by means of the mercury contact cups, C.

About 7 cc. of ester was used for each determination. A suitable rate of oxygen uptake (here, 0.1 to 1×10^{-5} mole O_2/min.) was arranged for by preliminary autoxidation or addition of benzoyl peroxide. After thermal equilibrium (as indicated by the galvanometer) had been established between the inside and outside of the calorimeter at about 40° C, oxygen at about atmospheric pressure was admitted; rapid mechanical shaking of the calorimeter ensured mixing of ester and oxygen; isothermal conditions inside and outside the calorimeter were maintained (to within 01.02° C) by means of manually-controlled resistance heaters immersed in the outer bath. Concurrent measurements were made of the temperature of the outer bath (using a Beckmann thermometer) and the oxygen uptake. Satisfactorily linear plots of these two measured quantities were in every case obtained throughout a temperature rise

of at least 5° C.   The apparent heat capacity of the calorimeter in this tem-
perature range was determined from the energy which had to be passed through
H to give a very similar rate of temperature rise in the calorimeter.   While
this procedure should eliminate errors due to conduction heat losses, it may be
noted that even for this unrefined design of calorimeter direct experimental
determination of the total heat losses showed that they were in any case less
than 1 per cent of the heat evolved by the oxidation.
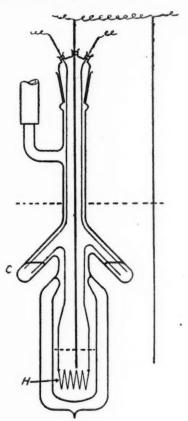
FIG. 1.—Calorimeter.

The final results obtained for the heat of oxidation of ethyl linoleate and
linolenate are summarized below.

	No. of deter-minations	Mean $-\Delta H$ k.cal.	D_{O-O} k.cal.
(a) Ethyl linoleate	5	53.3	66
(b) Ethyl linoleate + 0.4% benzoyl peroxide	2	52.5	65
(c) Ethyl linolenate	3	52.0	68

The mean deviation of each series was of the order of 1 k.cal.   The strength
of the O—O bond (D_{O-O}) is calculated[7] on the assumption that ethyl linoleate
contains 100 per cent of conjugated isomers[8] and ethyl linolenate 50 per cent[9].

RESONANCE ENERGIES[10]

According to the point of view developed in this paper, the effect of structure in modifying the reactivities of a series of related compounds is to be interpreted in terms of its effect on the resonance possibilities of the molecule and the radical derived from it.   Thus in a monoölefin, hydrogen atoms situated on the α-carbon atom are particularly labile, owing to the stabilizing effect of the resonance energy in the allyl radical

$$R.CH{=}CH.CH.R' \rightleftharpoons R.CH{-}CH{=}CH.R'$$

The stabilization is greatly increased in a 1, 3 or 1, 4-diene, either of which gives the radical:

$$R.CH{=}CH.CH{=}CH.CH.R'$$

The quantitative values employed here have been recalculated by Orr, following Coulson's method[11], and are as follows:

$$C{=}C{-}C{=}C \ 6.9 \text{ k.cal.}, \ C{=}C{-}C \ 18.7 \text{ k.cal.}, \ C{=}C{-}C{-}C{=}C \ 30.4 \text{ k.cal.}$$

The other important resonance possibility is that in a peroxide radical $R_2CH{-}O{-}O{-}$.   By analogy with Pauling's treatment[12] of the peroxide ion $O_2{-}$, this radical can be represented with a three electron bond, as $R_2CH{-}O{-}O{-}$ with, however, a charge displacement.   In view of this displacement, it seems unlikely that the bond can be nearly so strong in this case as in those considered by Pauling, in which the three-electron bond is taken to make a contribution equal to one-half the single bond strength.   Thus, instead of assuming a resonance stabilization of the radical of some 30 k.cal., we have quite arbitrarily taken 15 k.cal. as a more probable estimate.   In point of fact, none of the conclusions drawn below are seriously influenced by the value chosen.

THE POINT OF OXIDATIVE ATTACK IN OLEFINS

There are two possible sites for oxidative attack; the double bond, and an active methylene group.   In cases where a very high yield of α-methylenic hydroperoxide is obtained, it appears at first sight that the primary attack of oxygen must be at this point.   This argument is certainly invalid unless the chain length of the oxidation is extremely short.   Where a chain length of the order of 100 is found, as e.g., in ethyl linoleate, 99 per cent of the peroxide arises from the chain, and therefore gives no indication whatsoever as to the nature of the primary product.   The most likely formulations of the two modes of attack appear to be:

$$(a) \ \ R.\overset{\overset{\textstyle O_2}{|}}{C}H{-}\overset{|}{C}H.CH_2.R'$$

$$R.CH{=}CH.CH_2.R' + O_2$$

$$(b) \ \ R.CH{=}CH.\overset{|}{C}H.R' + HO_2{-}$$

The estimated heats of these two reactions are, for a monoölefin:

$$\Delta H_a = 145 + 118 - 81 - 87 - 66 - 15 = 14 \text{ k.cal.}$$
$$\Delta H_b = 99 + 118 - 19 - 110 - 66 - 15 = 7 \text{ k.cal.}$$

For a 1, 3-diolefin, attack at one end of the conjugated system is assisted by the development of allyl resonance

$$-\text{CH}-\text{CH}.\text{CH}=\text{CH}-$$
$$\mid \quad \mid$$
$$\text{O}_2$$
$$\mid$$

so that $\Delta H_a = 14 - 19 + 7 = 2$ k.cal.

The alternative path is also somewhat assisted by a greater gain of resonance energy: $\Delta H_b = 7 + 19 + 7 - 30 = 3$ k.cal. Double bond attack in a 1, 4-diolefin will be equivalent to that in a monoölefin, but α-methylenic attack will be easier by virtue of 11 k.cal. greater resonance energy in the radical ($\Delta H_b = -4$ k.cal.).

All of these reactions have heats lying below the energies of activation found experimentally, so none can be ruled out. Comparing the values found for the various olefins, we note that the order of reactivity by double bond attack is $1, 3 >$ mono- or $1, 4$; while for α-methylenic attack, $1, 4 > 1, 3 >$ mono. These two reaction paths are not mutually exclusive, and in principle we should expect both to proceed side by side, with one more or less predominant. An experimental determination of the absolute rates of the primary steps for the three types of olefin should throw light on the relative importance of the two reaction paths. Experimental work on this problem is now in progress, but is rendered very difficult by the smallness of the rates to be observed, and the relatively large disturbing influence of even small amounts of impurity.

THE NATURE OF THE PEROXIDES

In addition to α-methylenic hydroperoxides, oxidation frequently leads to peroxides of polymeric character[1], whose structure is less certain, but which appear to be relatively stable. Cyclic peroxides are also known, e.g., ascaridol, and are apparently formed directly in the oxidation of anthracenes[13]. We have, therefore, to consider how the various forms of peroxide can arise during the course of the oxidative chain reaction.

The kinetic evidence of the previous paper led to the view that hydroperoxides arise from the following chain cycle:

(c) $\text{R}.\text{CH}=\text{CH}.\text{CH}.\text{R}' + \text{O}_2 \rightarrow \text{R}.\text{CH}=\text{CH}.\text{CH}.\text{R}'$
$\qquad\quad \mid \qquad\qquad\qquad\qquad\qquad\qquad \mid$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \text{O}_2$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \mid$

(d) $\text{R}.\text{CH}=\text{CH}.\text{CH}.\text{R}' + \text{R}.\text{CH}=\text{CH}.\text{CH}_2.\text{R}' \rightarrow \text{R}.\text{CH}=\text{CH}.\text{CH}.\text{R}'$
$\qquad\quad \mid \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \mid$
$\qquad\quad \text{O}_2 \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \text{O}_2\text{H}$
$\qquad\quad \mid \qquad\qquad + \text{R}.\text{CH}=\text{CH}.\text{CH}.\text{R}'$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \mid$

Estimation of the heats of these reactions for the three types of olefins gives:

	mono-	1:3	1:4
ΔH_c	-31	-27[14]	-27[14]
ΔH_d	-15	-19	-26

These steps are clearly all so strongly exothermic as to be highly probable steps in a chain reaction. Reaction (d) is the one for which approximate energies of activation were deduced kinetically for ethyl linoleate and methyl oleate, the results being $E_{lin} > 4.2$, and $E_{oleate} - E_{lin} \simeq 4$, which appear quite consistent with the present estimates of ΔH.

There is no difficulty in seeing how the chain (c) + (d) could be initiated by a primary double bond attack, since the reaction:

$$(e) \quad R.CH-CH.CH_2.R' + R.CH=CH.CH_2R' \rightarrow R.CH-CH.CH_2R$$
$$\qquad\quad \underset{|}{O_2} \quad\; |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad O_2H$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad + R.CH=CH.CH.R'$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad |$$

would have the same heat of reaction as (d). Thus the reaction scheme put forward in the previous paper is completely satisfactory thermochemically. Taken in conjunction with its complete agreement with the chemical, spectroscopic and kinetic evidence, this affords valuable confirmation of its probable correctness.

We now wish to show how alternative reactions of the radicals which participate in this scheme can lead to different final products. Except at low pressures, the chain length of all the oxidation chains discussed in the previous paper is determined by the relative rates at which RO_2—radicals react: (1) with a molecule of olefin and (2) with other RO_2—radicals. Just as oxygen might attack either a double bond or an active methylene group, so it is to be anticipated that a further possible reaction of a peroxide radical would be with a double bond:

$$(f) \quad RCH-CH.CH_2R' + RCH=CH.CH_2.R' \rightarrow R.CH-CH.CH_2R'$$
$$\qquad\quad \underset{|}{O_2} \quad\; |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \underset{|}{O_2}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad R.CH-CH.CH_2R'$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$

The free radical ends would then react with oxygen (as in (c)), producing further peroxide radicals which could again add olefin, thus building up a polymeric chain in which the repeating unit is:

$$-CH(CH_2R').CHR.O_2-$$

In the case of a conjugated olefin, addition could also take place across the terminal carbons of the system, giving:

$$-[CHR.CH=CH.CHR'.O_2]_n-$$

Estimation of the heat of reaction ΔH_f for various olefins gives: mono-, -8; 1, 3, -20; 1, 4, -8. This step is alternative to (e) and it is clear that the probability of a polymeric chain is highest for conjugated olefins and least for 1, 4 dienes; it is in very satisfactory agreement with this conclusion that it is in fact conjugated olefins which display a high tendency to yield polymeric peroxides, while ethyl linoleate and methyl oleate have been found to give quantitatively hydroperoxide.

Reaction (f) represents the formation of polymer from a peroxide radical derived by double bond attack, but it is clear that a similar reaction could occur,

with the same ΔH, with an α-methylenic peroxide radical.   Hence, even in a reaction chain leading normally to hydroperoxide, occasional linking of two or more molecules can occur by this mechanism.   Conversely, at any stage of the polymerization, growth of the polymer can be terminated by the intervention of Reaction (e).   It is important to note that this would not constitute a termination reaction in the kinetic sense, since the number of free radicals remains unchanged.   Reaction (e) in this way would function as a "transfer" reaction[15], and the kinetic chain length could be considerably greater than the average degree of polymerization.   Although we have at present no kinetic data for conjugated systems, the relatively low molecular nature of the polymers reported[1] suggests that this may well be the case.

It is interesting to compare the kinetics of a chain leading to hydroperoxide with those of a polymeric chain of the type suggested here.   This kinetic problem can be treated very simply on the assumption that the reactivities of radicals are independent of the size of polymer to which they are attached. Formally the reaction sequence may then be written (with RH for the olefin, R— for any hydrocarbon radical and RO_2— for any peroxide radical):

$$RH + O_2 \xrightarrow{k_8} R— + RO_2— \; (i.e. \; —RHO_2—)$$
$$R— + O_2 \xrightarrow{k_2} RO_2—$$
$$RO_2— + RH \xrightarrow{k_9} R—$$
$$2RO_2— \xrightarrow{k_6} \text{stable products}$$
$$\cdots \cdots \cdots \cdots \cdots$$
$$RO_2— + RH \xrightarrow{k_3} RO_2H + R—$$

Reactions (8), (2), (9) and (6) form the polymerization chain; (3) a reaction, alternative at any stage to (9), which yields hydroperoxide.   By writing down stationary state equations for the total concentration of the two types of free radicals, it is readily shown that:

$$- \frac{d[O_2]}{dt} = (k_3 + k_9)(2k_8/k_4)^{\frac{1}{2}}[RH]^{\frac{1}{2}}[O_2]^{\frac{1}{2}}$$
$$\frac{d[RO_2H]}{dt} = k_3(2k_8/k_4)^{\frac{1}{2}}[RH]^{\frac{1}{2}}[O_2]^{\frac{1}{2}}.$$

The conclusion is that reactions leading to hydroperoxide and to polymer would be kinetically indistinguishable.

One other type of peroxide which should be considered is a cyclic structure, forming a ring of either 4 or 6 members.   The former, which has been widely suggested[16], could readily arise from cyclization of the primary peroxide radical:

$$(g) \quad R.CH.CH.R' \longrightarrow R.CH—CH.R'$$

Although this reaction would be strongly exothermic ($\Delta H_g \simeq -70$), at least two factors militate against its importance: (1) the geometrical improbability of 4 membered rings[17], and (2) the great ease with which the hydrocarbon radical reacts with oxygen.   It is doubtful whether peroxides of this structure would be isolable, even if formed, since it is easily shown that the simultaneous rup-

ture of C—C and O—O bonds to give RCHO + R′CHO would be exothermic by some 27 k.cal. Scission reactions based on the breakdown of such rings have been suggested[18]. Stable six membered rings might well be formed by this process from conjugated diolefins, particularly at low oxygen pressures and in dilute solution, so competing reactions are retarded:

(h) R.CH.CH=CH.CH.R $\longrightarrow$ R.CH$\overset{\overset{\displaystyle CH=CH}{\diagup}}{\underset{\underset{\displaystyle O——O}{\diagdown}}{}}CHR_1$ ($\Delta H_h = -53$)
　　|
　　O$_2$
　　|

Less facile ring-closure reactions are also to be expected from an intramolecular equivalent of reaction (f), for example:

(i) R.CH—CH.CH$_2$.CH=CH.R $\longrightarrow$ R.CH—CH$\overset{\overset{\displaystyle CH_2-CH}{\diagup}}{\underset{\underset{\displaystyle O——O}{\diagdown}}{}}$CHR
　　　|
　　　O$_2$
　　　|

or, in 1, 5 dienes:

(j) RCH=CH.CH.CH.CH=CHR $\longrightarrow$ R.CH=CH.CH$\overset{\overset{\displaystyle CH_2-CH}{\diagup}}{\underset{\underset{\displaystyle O——O}{\diagdown}}{}}$CHR
　　　　|
　　　　O$_2$
　　　　|

The relative importance of these various processes is at present completely unknown.

HYDROCARBON POLYMERS

Another possibility to be borne in mind in considering the oxidation of olefins is that of the production of hydrocarbon polymers, for which oxygen is known to be a catalyst. Hitherto, we have in effect assumed that every hydrocarbon free radical produced reacts with oxygen. Clearly an alternative to this is an addition of the radical at a double bond, the typical chain-propagation step in olefin polymerization, for example:

(k) R.CH.CHR′— + RCH=CHR′ $\longrightarrow$ RCH.CHR′.CHR.CHR′—
　　　|　　　　　　　　　　　　　　　　　　　　|
　　　O$_2$　　　　　　　　　　　　　　　　　　 O$_2$
　　　|　　　　　　　　　　　　　　　　　　　　 |

The calculated heat of this reaction for various olefins is −17 k.cal. (mono- or 1, 4), −10 k.cal. (1, 3). Its exothermic character means that it will always be a possibility to be seriously considered, particularly at low oxygen pressures.

It is to be noted that an α-methylenic free radical is much less likely to promote polymerization, the estimated heats of reaction for addition to a double bond being 2 k.cal. (mono-), 1 k.cal. (1, 3) and 6 k.cal. (1, 4).

The interrelation between the chain processes leading respectively to polymeric peroxide and to hydrocarbon polymer suggests some interesting possibilities. In the first place it is clear that incorporation of oxygen followed by

addition of olefin (Reaction (f)) represents a double step which is substantially equivalent to Reaction (k) and gives a similar free radical.   It follows that the two alternative processes can proceed consecutively, giving rise to a range of polymers whose oxygen content is determined by the oxygen pressure.   This dual polymerization is interrupted if at any stage the peroxide radical reacts by path (e), thus terminating the polymer growth by the formation of a hydroperoxide end.   The possibilities thus envisaged do not appear to have been seriously investigated.   Although Medvedev and Zeitlin[19] have shown the production of a considerable amount of high polymer to accompany the thermal oxidation of styrene, they unfortunately do not report the effect of oxygen pressure on either the yield or oxygen content of the polymer.

OXIDATION OF POLYISOPRENES

To the approximation employed above, polyisoprenes are treated as assemblies of isolated double bonds.   Since the ultimate objective of our work is the understanding of polyisoprene oxidation, it is desirable to discuss this system in a little more detail.   The essential reactive system is a methyl substituted 1, 5 diene unit:

$$RCH_2.C(CH_3):CH.(CH_2)_2C(CH_3):CH.CH_2R.$$

The reactivity to oxygen or peroxide radicals of the double bonds in any olefin is enhanced by methyl substitution on the double bond, owing to stabilization of the resulting radicals by the contribution of such forms as:

$$\begin{array}{c} HCH_2 \\ \| \\ R.\overset{}{C}.CHR.O_2- \end{array}$$

Two consequences may be expected to follow: (1) an increased rate of oxidation, and (2) a greater tendency to polymer formation, compared to the unsubstituted olefin.   We have at present no experimental data bearing directly on this point.

Strong evidence has also been advanced[20] in support of the view that the central bond in 1, 5 diene systems is considerably strengthened by a hyperconjugation involving the two methylene groups.   This would tend to reduce the α-methylenic reactivity of the molecule, but since similar possibilities exist in the α-methylenic radicals, it is difficult to predict the resultant effects.

Comparing squalene with a typical monoölefin, methyl oleate, there is some indication both of increased oxidizability and of greater ease of polymerization.

SUMMARY

A new estimate of the O—O bond strength in hydroperoxides is reported, based on a determination of the heats of oxidation of ethyl linoleate and linolenate.

This value is employed, together with other known bond strengths and resonance energies, to estimate the heats of a number of alternative oxidation reactions of olefins.   By considering the effects of the olefin structure on these heats of reaction, it is possible to see how structural differences can lead to the formation of different oxidation products.   The discussion is confined to primary products of the oxidation chain, but, even so, a considerable diversity of

behavior is shown to be possible. The final material may include simple monomeric hydroperoxides, polymers with varying amounts of oxygen incorporated in the chain, cyclic peroxides, and scission products. The very limited experimental evidence available falls generally into line with expectation.

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SULFUR BOND IN VULCANIZATES
IMPLICATIONS OF HALOGEN REACTIONS*

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The chemistry of vulcanization was investigated with renewed interest after the demonstration by Farmer[1] of the generality of α-methylenic reactivity in olefinic systems. Selker and Kemp[2] and Armstrong, Little, and Doak[3] produced independent evidence of allylic type sulfide bonds in vulcanizates and in the reaction products of sulfur and simple olefins; this supports the α-methylenic mode of attack in sulfur vulcanization. Armstrong and his coworkers suggested likely secondary reactions and final vulcanizate structures based on analogies with simpler systems.

The investigations by the writers, during the past few years, of the reactions of vulcanization and the chemical behavior of vulcanized products corroborates the previous findings with regard to α-methylenic reaction and provides a more detailed analysis of the secondary reactions in various vulcanizing systems. The results to date are presented in two papers; the first concerns the reaction of vulcanizates with iodine chloride and bromine, and the second, the further investigation of mineral sulfide formation as an index of the type of sulfur bonding.

The object of the first paper is to consider the significance and implications regarding the vulcanizate structure of the reaction between sulfur-vulcanized polyprenes and the halogens, iodine chloride and bromine, respectively, under conditions simulating the various common methods of analyzing rubber for double bonds. The reaction under these conditions includes both the addition of halogen to double bonds and, in the case of iodine chloride, the formation of halogen acid in proportion to the sulfur present—presumably by a sulfur-induced process. The behavior under similar conditions of a number of simple sulfur compounds including propyl sulfide, dodecyl sulfide, propyl disulfide, allyl sulfide, methallyl sulfide, and butylmethallyl sulfide was also observed, and analogies with the vulcanizates are indicated.

Iodine chloride was employed by others in the manner suggested by Kemp and his coworkers[4] to follow vulcanization stoichiometrically by relating the combination of vulcanizing agent to loss in unsaturation; this approach was applied to both sulfur and nonsulfur vulcanizations. Brown and Hauser[5], employing the Kemp-Wijs method as modified by Blake and Bruce[6], confirmed the early conclusions of Spence and Scott[7] with regard to simple rubber-sulfur vulcanizates—namely, that one double bond is consumed per sulfur atom in the vulcanization reaction. Applying their technique to several typical accelerated gum stocks, Hauser and Brown concluded that the latter undergo considerably less change in unsaturation with combination of sulfur. They

associated the smaller change in unsaturation with a change in mechanism effected by the accelerator. However, their few tests on vulcanizates with zinc oxide in the absence of organic accelerator showed a similar departure from the results obtained with the simple rubber-sulfur stocks. No data were reported for stocks vulcanized with organic accelerators in the absence of zinc oxide. Thornhill and Smith[8], studying reinforced vulcanized rubbers, found results similar to those of Hauser and Brown. In fact, certain well cured carbon black stocks were observed to have undergone negligible changes in iodine number as a result of the cure.

No mention is made of possible sulfur-induced reactions arising from the treatment of vulcanized products with halogens and their bearing on the determination of unsaturation previous to the recent paper of Bloomfield[9]. The authors are pleased to acknowledge this latest of several important contributions by Bloomfield to the field of rubber halogenation, and are gratified to note several conclusions in common with the findings of this investigation, despite a somewhat different point of view. The review of Connor[10] cites a variety of reactions in which sulfur compounds of various types are either oxidized directly by halogens or act as carriers to promote halogenation reactions. In the course of the present studies it was found that sulfur combined in vulcanizates does profoundly affect the reaction with iodine chloride.

EXPERIMENTS WITH VULCANIZATES

General Procedure.—The stocks were compounded on a small laboratory mill and cured in a laboratory steam-heated press. Combined sulfur was calculated as the difference between sulfur compounded and free sulfur, as measured by sodium sulfite extraction[11]. These values were checked in a number of cases by determining combined sulfur directly on the acetone-extracted residue.

Samples of both cured and uncured stocks were extracted with acetone for about 20 hours, dried in vacuo at 70° C for 2 hours, and analyzed for unsaturation by the procedure described by Kemp and Peters[12], with variations in halogen, solvent for halogen, time, temperature, and sample weight, as indicated. Blank determinations were run with each new set of conditions. Halogen acid was determined where possible by the well known method of McIlhiney[13].

Details of the analytical method follow. The acetone-extracted residue, after removal from the drying oven, was cooled in a vacuum desiccator, weighed (0.1 gram unless otherwise indicated) into a 500-cc. iodine flask, and dissolved by heating in 50 grams of p-dichlorobenzene for the minimum time required to effect solution. The solution was partially cooled, diluted with 50 cc. of U.S.P. chloroform, and finally brought to the desired reaction temperature. Twenty-five cc. of approximately 0.2 N halogen (iodine chloride or bromine) in carbon tetrachloride or glacial acetic acid was mixed into the solution by gentle swirling, and the flask was placed in a bath in darkness. After the desired reaction time the solution was shaken with 25 cc. of 15 per cent potassium iodide and titrated with 0.1 N sodium thiosulfate; 5 cc. of 1 per cent starch in 15 per cent sodium chloride solution was added shortly before the end point was reached. Alcohol was introduced as needed during the titration to break emulsions. When carbon tetrachloride was used as the halogen solvent, 10 cc. of 5 per cent potassium iodate solution was introduced after the first end point,

and the mixture was finally titrated to a second end point with thiosulfate in order to obtain a measure of hydrogen halide.

When glacial acetic acid was used as the halogen solvent, the hydrogen halide was determined as halide ion by reducing the excess halogen to halide with sodium sulfite, determining the total halide by the Volhard method, and subtracting the halide due to free halogen. The special procedure used for the acetic acid system may be described as follows. After the specified reaction period, one sample was titrated with thiosulfate, as described. To a second sample were added 50 cc. of water and then approximately 0.1 N sodium sulfite from a buret until the excess halogen was exactly reduced (end point detected by change of color of the nonaqueous layer). The aqueous layer was separated in a separatory funnel and the nonaqueous layer washed three times with 30-cc. portions of water; emulsions were broken by adding alcohol. The aqueous extracts were combined with the original aqueous layer and acidified with 5 to 10 cc. of 6 N nitric acid; the slight iodine color which appeared was destoryed by a drop or two of sodium sulfite. A measured excess of 0.1 N silver nitrate was added, and the total halide was determined by the Volhard method in the presence of nitrobenzene[14]. Free halogen and total halogen were determined similarly on a blank.

To determine the fate of the respective halogens (iodine and chlorine), a 10 per cent aliquot part of the aqueous extracts after sodium sulfite reduction was analyzed separately for iodide according to the method of Kolthoff and Sandell[15]. The sample was neutralized by adding dilute sodium hydroxide in the presence of an indicator, and then made slightly acid with a drop of acetic acid before oxidation with bromine. The oxidized solution was finally made distinctly acid with 20 to 30 cc. of 1 N hydrochloric acid before titration of the iodate with thiosulfate.

Method of Calculation.—Iodine numbers, hydrogen halide, and combined sulfur are based on 100 grams of the raw elastomer as compounded. For convenience in showing stoichiometric relations, the results are expressed as millimoles of halogen consumed and of hydrogen halide formed, and milliatoms of sulfur combined per 100 grams of elastomer.

Combined sulfur, S_c, in grams per 100 grams of elastomer, is given by $S_0 - (S_f W/100)$, where S_0 represents sulfur compounded, S_f is the percentage of free sulfur found in the sample, and W is the total parts of ingredients per 100 parts of elastomer.

Since halogen tests are made on acetone-extracted samples, the observed iodine numbers (or other expressions of unsaturation based on a given sample weight) and acid values are corrected to the basis of elastomer by multiplying by $(100 - E)W/10,000$, where E is the percentage extract in the vulcanizate (or uncured mixture).

Iodine numbers represent the total halogen consumed in the test, without regard to the fate of the halogen. That is, no attempt is made to correct iodine number for halogen consumed in extraneous reactions such as substitution. The term "iodine number", therefore, is equivalent throughout this paper to the term "apparent unsaturation".

Since the investigation is concerned principally with changes resulting from the combination of sulfur, the data for apparent unsaturation U are plotted as U_k, the difference between an arbitrarily selected zero representing the best unsaturation value for the raw elastomer (iodine number of 350) and the experimentally observed value. This method of plotting shows any changes in

unsaturation values of uncured elastomers due to changes in test conditions, as well as the relative values for the cured and uncured stocks under any given set of conditions.

Preliminary Results with GR-S.—A number of GR-S gum formulas were vulcanized, acetone-extracted, and treated with iodine chloride in carbon tetra-

<div align="center">TABLE I</div>

<div align="center">APPARENT UNSATURATION AND ACID PRODUCTION IN ANALYSIS OF GR-S VULCANIZATES
WITH IODINE CHLORIDE IN CARBON TETRACHLORIDE*</div>

| Stock | Time of cure at 145° C (hrs.) | Iodine no. | HX, millimoles per 100 grams GR-S | | Combined sulfur (milliatoms per 100 grams) GR-S |
			Total	Incremental†	
A	0	319	94	..	..
	3	318	108	14	12.5
	6	317	138	44	28.0
	8	310	166	72	44.8
	14	311	200	106	60.7
B	0	325	98	..	..
	2	325	128	30	15.9
	4	322	164	66	31.5
	8	312	304	206	109
	12	309	350	252	114
C	0	324	34	..	..
	0.25	323	44	10	19.0
	0.5	322	158	124	62.6
	1	323	160	126	63.0
	2	321	166	132	64.5
D	0	324	50	..	..
	0.25	328	274	224	108
	0.5	330	292	242	115
	1	324	286	236	115
	2	322	308	258	116
E	0	312	50	..	..
	0.25	316	450	400	209
	0.5	316	504	454	234
	1	316	546	496	237
	2	311	538	508	240

* Reaction time, one hour at room temperature.
† Obtained by subtracting acid for uncured stock from total acid.

chloride for 1 hour at room temperature (Table I). The formulas were as follows:

Formula	A	B	C	D	E
GR-S	100	100	100	100	100
Sulfur	2	4	2	4	8
Zinc oxide	..	..	3	3	3
Santocure	..	..	1.2	1.2	1.2

Under these test conditions even the unaccelerated GR-S vulcanizates showed little change in iodine value with increasing combined sulfur. This would suggest that either no loss in unsaturation occurred during vulcanization, or that substitution reactions or reactions of halogen with sulfur largely compensated for loss of unsaturation, and resulted in approximately constant halogen consumption.

Figure 1 shows the acid formed during the test plotted as a function of combined sulfur. The simple relation between acid and combined sulfur (2HX per sulfur atom) suggested the acid-forming reaction as a means for characterizing the sulfur linkage of vulcanization based on its ability to reduce iodine chloride. Parallel studies of typical sulfur compounds of known structures would serve as a guide for interpretation of the behavior of the vulcanizate systems. It was believed that such a technique, in conjunction with iodine number determination, would be of considerable value. However, the determination of unsaturation in GR-S was found to be too erratic for the purpose, particularly in view of the uncertainty in the uncured stocks.

On the other hand, natural rubber presented no such obstacle, since iodine chloride had proved to be a reliable reagent for raw rubber. Moreover, it seemed desirable to check previous results with rubber-sulfur vulcanizates, with particular attention to formation of acid in the unsaturation test mixture.
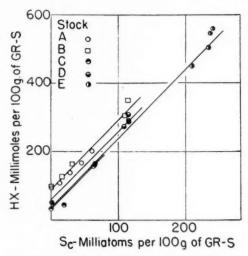
FIG. 1.—GR-S stocks of Table I, iodine chloride.

Experiments with Natural Rubber.—The simple rubber-sulfur formula of pale crepe 100, sulfur 8, which was studied by Brown and Hauser[16], was selected for further investigation. The mixture was cured 2, 4, 6, and 8 hours at 141° C—a typical set of cures containing 1.57, 3.53, 5.77, and 6.90 grams combined sulfur, respectively, per 100 grams of pale crepe. The cured stocks as well as the uncured mixture were acetone-extracted, dried in the vacuum oven, and analyzed for apparent unsaturation and hydrogen halide formation as described.

The first experiments were carried out with the usual 0.1-gram sample and 25 cc. of approximately 0.2 N iodine chloride. The sample was ordinarily dissolved by heating in *p*-dichlorobenzene, followed by dilution with U.S.P. chloroform or c.p. carbon disulfide as described. However, one set of samples was treated after mere swelling in dichlorobenzene-chloroform mixture for 22 hours at room temperature; the results are fairly comparable to those obtained after complete solution by the standard treatment (Figures 2 and 3).
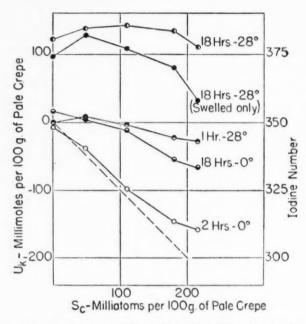
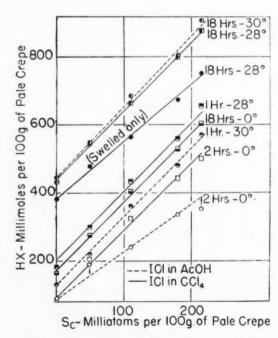FIG. 2.—Pale crepe-sulfur, 0.1-gram sample, iodine chloride in carbon tetrachloride.

FIG. 3.—Pale crepe-sulfur, 0.1-gram sample, iodine chloride.

Time and temperature conditions were varied; they gave the apparent unsaturation values plotted against combined sulfur in Figures 2 and 4.

The variously determined iodine numbers (right-hand scale of ordinates) of the uncured stocks are in good agreement for both carbon tetrachloride and glacial acetic acid solutions of iodine chloride, except in the 18-hour tests at room temperature, where a great deal more halogen is consumed—probably because of substitution.   The increase in HX as a result of the increased reaction time amounts to two or three times the increase in U_k (Figures 2, 3, and 4); most of this increased HX formation necessarily results from reactions other than substitution—for example, from dehydrohalogenation of the type proposed by Bloomfield[17], wherein an activated dihalide may form, through loss of HX, either a halogenated olefin (that is, C=C—Cl, which would add iodine
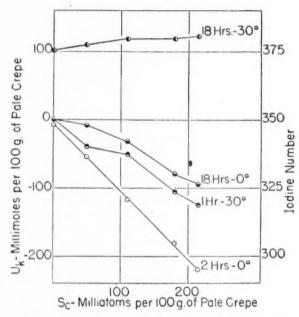
Fɪɢ. 4.—Pale crepe-sulfur, 0.1-gram sample, iodine chloride in glacial acetic acid.

chloride with difficulty) or a cyclized monohalide.   In agreement with the previous work of Kemp and Mueller[18], the use of 1-hour reaction time at room temperature appears to be justified as an expedient in the analysis of raw rubber.

However, the divergence of the curves with increasing sulfur (Figures 2 and 4) shows a remarkable sensitiveness of the vulcanizates to test conditions. Thus, only the 2-hour test with glacial acetic acid reagent at 0° C gave $-\Delta U/\Delta S_c$ equal to unity, in agreement with the findings of Brown and Hauser; all the other test conditions gave values less than unity.   Except for the 1-hour tests at room temperature, the results with glacial acetic acid and carbon tetrachloride, respectively, under comparable conditions, are fairly similar.

The slopes of the acid curves (Figure 3) are surprisingly independent of reaction conditions (except 2 hours in acetic acid), amounting to about 2 hydro-

gen halide molecules per sulfur atom, in spite of the variations in absolute acid values already discussed. Assuming the HX obtained with raw rubber under given test conditions to be a constant component of the total HX obtained with the vulcanizates, one may interpret the linear relation between HX and S_c as evidence of one or more acid-forming reactions which are directly influenced by the combined sulfur, and which are essentially independent of other HX-producing reactions.

Seeking a limiting slope in the halogen consumption curve ($\Delta U/\Delta S_c$), the authors attempted to increase the halogenation rate by increasing the halogen-sample ratio—that is, by reducing the size of sample. The effect of decreasing the sample to 0.07 gram, all other amounts remaining the same, is shown in Figure 5. With the smaller sample the results show negligible loss or even a
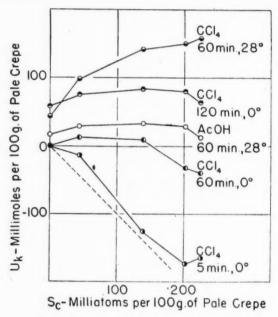
Fig. 5.—Pale crepe-sulfur, 0.07-gram sample, iodine chloride.

gain in unsaturation, except in the curve representing 5-minute reaction at 0° C; in the latter case, the slope agrees fairly well with the results of Brown and Hauser. The production of hydrogen halide (Figure 6) equals or exceeds 2 hydrogen halide molecules per sulfur atom (except for the 5-minute curve) but still bears a linear relation to sulfur after an inexplicable initial steep rise. Similar results, with still higher halogen consumption and acid formation, were obtained with 0.05-gram samples.

Under mild conditions, on the other hand, some consistency appears in the unsaturation results; this suggests an approach to a limiting curve corresponding to the relation of one double bond consumed per sulfur atom (found by Hauser and Brown and confirmed in the present work) with iodine chloride in acetic acid, in a 2-hour reaction at 0° C. The unsaturation curves, shifted for comparison to a common origin on the ordinate scale, are replotted in Figure 7.
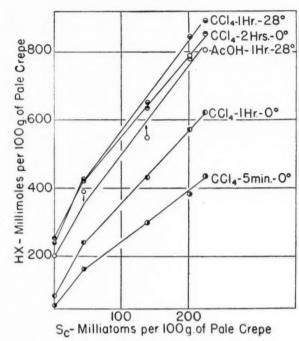
FIG. 6.—Pale crepe-sulfur, [0.07-gram sample, iodine chloride.

The HX slopes under the mild conditions vary considerably (Figure 8, curves similarly shifted to a common origin). This makes the significance of these tests questionable also as a criterion of true unsaturation.

Thus, the use of iodine chloride for determining the unsaturation of vulcanized stocks is of questionable reliability, and the reaction is of interest here
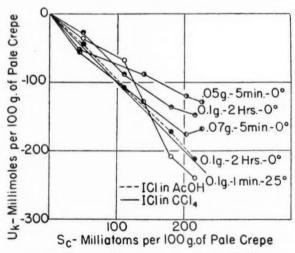

FIG. 7.—Pale crepe-sulfur, mild conditions, iodine chloride.

only as a means of establishing a behavior pattern for comparison of the vulcanizates with simple, known sulfur compounds. The significance of such comparisons will be considered later.

A feature of the sulfur-induced halogenation reaction which supplies important evidence of the nature of the sulfur bond is its selectivity for chlorine. When iodine chloride is added to uncured rubber under mild test conditions (for example, glacial acetic acid reagent, 2 hours at 0° C), no color change takes place other than a dilution effect. However, the same treatment of vulcanized rubber produces a marked change from dark reddish-brown to purple, which indicates liberation of free iodine. It was of interest to establish whether the selective reaction promoted by the combined sulfur results in stable combination of chlorine (in excess of iodine) in the rubber chain. Stable chlorine-to-carbon linkages would result, for example, from selective substitution, addition of chlorine, addition of iodine chloride followed by elimination of hydrogen iodide, or hydrolysis of an iodide bond. Selective reaction without stable
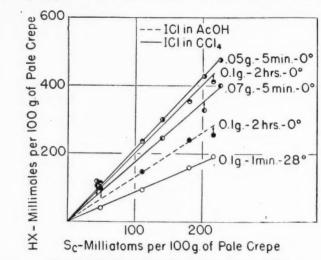
FIG. 8.—Pale crepe-sulfur, mild conditions, iodine chloride.

combination of chlorine, on the other hand, would result from hydrolytic oxidation of a sulfur atom—for example, oxidation of an alkyl sulfide to a sulfoxide—and lead to the attachment of oxygen to sulfur and the reduction of iodine chloride to iodine and hydrogen chloride. (Any hydrogen iodide formed as a result of such a reaction would immediately react with excess iodine chloride to form molecular iodine and hydrogen chloride.) Results of the present work, obtained by analyzing the aqueous phase of the reaction mixtures for the individual halogens, show that a disproportionate amount of chlorine (compared to iodine) becomes stably bound with the vulcanizate molecule and that the extent of such selective combination is in direct proportion to the sulfur present (Figure 9). Furthermore, the excess chlorine is approximately equivalent to the hydrogen halide formed under the respective conditions (Figure 4)—that is, one atom of chlorine equivalent to one molecule of hydrogen halide. This suggests strongly that the source of incremental acid due to the presence of sulfur in the vulcanizates may be one or more of the following reactions, enhanced by the presence of the sulfur bond: selective substitution, addition of iodine chloride followed by loss of hydrogen iodide, or hydrolysis of iodide

linkages.   Moreover, one may infer that the sulfur bond is not of the type which would readily undergo hydrolytic oxidation by halogens.

Bromine Reaction with Rubber Vulcanizates.—Bromine, under proper reaction conditions, proved more satisfactory than iodine chloride as a means for measuring the unsaturation or vulcanized samples.   Recently a bromine addition agent, pyridine sulfate dibromide ($C_5H_5N \cdot H_2SO_4 \cdot Br_2$), catalyzed by mercuric acetate, was reported[19] to react with crude tall oil exclusively by addition; secondary substitution reactions were negligible after a 23-day reaction period.   This reagent without the mercury catalyst (previous experiments had shown that mercuric ion gave very high, inaccurate iodine values) was applied to the rubber-sulfur vulcanizates under investigation.   The results corroborated those found with iodine chloride in glacial acetic acid at 0° C and 2-hour reaction time, and tended to confirm the relation found by Brown and Hauser. Hydrogen halide was not determined.
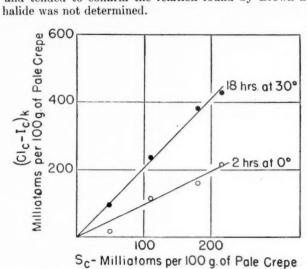
FIG. 9.—Pale crepe-sulfur, 0.1-gram sample, iodine chloride in acetic acid.

Bloomfield[17] reported bromine in chloroform to be a satisfactory reagent for determining the unsaturation of raw rubber.   However, the writers found bromine to be more stable in carbon tetrachloride than in chloroform, and obtained equally satisfactory results in analyzing rubber samples dissolved in chloroform-dichlorobenzene mixtures.   Therefore, they conducted a series of tests on the vulcanizates with 0.2 N bromine in carbon tetrachloride and obtained results which are surprisingly free of the complicating sulfur-induced reaction observed with iodine chloride.   The outcome of the tests (Figure 10) is believed to be significant not only in confirming the $\Delta U/\Delta S_c$ ratio of unity, but also in indicating characteristic features of the structure of the vulcanizate.

The striking feature of the results with bromine, in contrast to those with iodine chloride, is that the halogen acid formed is unaffected by combined sulfur, although the actual values for HX formed on treating uncured rubber with bromine are several times greater than those obtained with iodine chloride. In view of the agreement of iodine numbers of the raw rubber obtained by the two respective reagents, the greater acid production with bromine is believed to result from a greater degree of hydrolysis or dehydrohalogenation in the case of the bromine addition product.   This suggests that one or both of

these reactions occur more rapidly in the case of a *tert-sec*-dibromide than in the case of a *tert*-chloride–*sec*-iodide. Acid-forming reactions evidently increase with decreasing sample weight, but the extent of these reactions appears to remain constant with increasing combined sulfur, since virtually no increment in HX is observed. Change in sample weight is shown to have no substantial effect on $\Delta U/\Delta S_c$, as shown by the parallel curves of slope indicating the loss of one double bond per sulfur atom combined.
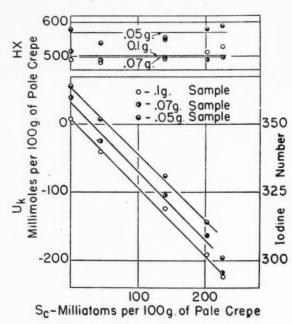
FIG. 10.—Pale crepe-sulfur, bromine, 2 hours at 0° C.

Action of Bromine on GR-S Vulcanizates.—The bromine method for unsaturation was found to be unreliable for GR-S vulcanizates. Low iodine values were obtained even with uncured samples in comparison with iodine chloride (Table II). As with natural rubber, sulfur-induced halogenation, forming HX,

TABLE II

ACTION OF BROMINE AND IODINE CHLORIDE ON GR-S VULCANIZATES
(Formula: GR-S, 100; S, 8)

Time of cure at 145° C (hrs.)	0	2	4	6
Combined sulfur (milliatoms per 100 g. GR-S)	..	58	114	161
Iodine value on GR-S				
ICl in CCl₄, 2 hrs. at 0° C	311	297	287	274
ICl in CCl₄, 1 hr. at 34° C	322	328	319	308
Br₂ in CCl₄, 2 hrs. at 0° C	291	281	286	268
Br₂ in CCl₄, 1 hr. at 28° C	300	294	292	292
Halogen acid (millimoles per 100 g. GR-S)				
ICl in CCl₄, 2 hrs. at 0° C	104	198	288	392
ICl in CCl₄, 1 hr. at 34° C	102	226	414	552
Br₂ in CCl₄, 2 hrs. at 0° C	224	256	246	316
Br₂ in CCl₄ 1 hr. at 28° C	222	224	306	372

is relatively greater with iodine chloride, although not entirely absent with bromine. This suggests that the form of combined sulfur is similar though not identical to that in rubber-sulfur stocks.

Effect of Accelerators and Zinc Oxide on Loss of Unsaturation in Vulcanization of Rubber.—The pale crepe-sulfur formula was augmented by organic accelerators, zinc oxide, or both, to determine the effects on the type of sulfur combination as reflected in the analyses with bromine.

The effect of organic accelerators alone is shown in Figure 11. The points represent successive cures up to 2 hours at 141° C, when, except in the case of the Monex stock, substantially all of the sulfur has combined. Thus, D.O.T.G., A-808, Captax, and Santocure all catalyze the combination of sulfur to a marked degree, even in the absence of zinc. However, it is evident from the slope of the curve relating unsaturation to combined sulfur that the presence of the
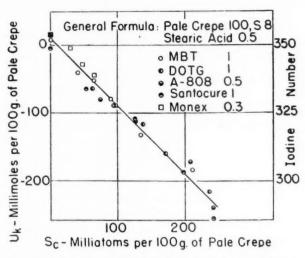
FIG. 11.—Pale crepe-sulfur-organic accelerator, bromine, 2 hours at 0° C.

organic accelerators without zinc causes no essential change in the form of sulfur combination. That is, the loss of unsaturation is approximately one double bond per sulfur atom, as in the unaccelerated reaction.

The presence of zinc, on the other hand, appears to cause a different type of sulfur combination, even in the absence of organic accelerators; this results in a smaller loss of unsaturation (Figure 12). The corrections in the points for the D.O.T.G. and Captax stocks, indicated by arrows, result from deducting zinc sulfide sulfur from total combined sulfur and, at the same time, reducing the ordinates by a like amount on the assumption that a mole of zinc sulfide consumes a mole of halogen in accordance with the approximate relation found with c.p. zinc sulfide. The applied corrections, although possibly on the high side, still leave a gap between the data for zinc and nonzinc, and indicate a real difference in a part of the sulfur reaction in the presence of zinc. (Reaction of zinc sulfide with bromine should give sulfur and zinc bromide, which could conceivably lead to loss of unsaturation by direct action on the rubber chain, and thus compensate in part the consumption of halogen by zinc sulfide.)

The effect of zinc is in line with the α-methylenic theory of Farmer[1] and with the suggestion of Armstrong, Little, and Doak[3] that an intermediate thiol formed in the initial stages of vulcanization may react with the metal soap to give a mercaptide which, on further reaction, is converted to a thioether or disulfide with simultaneous formation of metal sulfide. Such a reaction would explain the lower loss of unsaturation, since no double bonds would be lost in the process. Presumably the type of vulcanization obtained in the absence of metals would proceed simultaneously, in which case the relative dominance of the two types of vulcanization would determine the unsaturation.
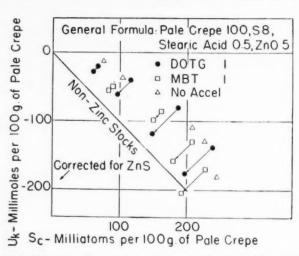
Fig. 12.—Pale crepe-sulfur-organic accelerator—zinc, bromine, 2 hours at 0° C.

SULFUR COMPOUNDS OF LOW MOLECULAR WEIGHT

The following simple sulfur compounds were investigated: propyl sulfide, dodecyl sulfide, propyl disulfide, allyl sulfide, methallyl sulfide, and butyl-methallyl sulfide. The propyl sulfide, allyl sulfide, and propyl disulfide were Eastman chemicals; their purities were checked by determination of refractive indices, which agreed well with the published values of Selker and Kemp[2]. The dodecyl sulfide was a product of the Connecticut Hard Rubber Company (melting point after recrystallization, 39.5° C).

Butylmethallyl sulfide was synthesized from butanethiol and methallyl chloride according to the method of Bost and Conn for propyl sulfide[20]. Yield, 53 per cent of butyl methallyl thioether; b.p., 68–71° C at 14.5–15 mm.; n_D^{21}, 1.4687; d_4^{20}, 0.8636; MR_D (molecular refraction) observed, 46.45, calculated, 46.90 [using atomic refraction for thioether sulfur of 7.97[21]].

Methallyl sulfide was prepared by treating methallyl chloride with flake sodium sulfide (Hooker Electrochemical Company, 60 per cent sodium sulfide) in alcohol. The reaction was vigorous and had to be cooled in the early stages. The product was washed with water and sodium hydroxide, dried over anhydrous calcium sulfate, and distilled under vacuum (b.p., 59–60° C at 10 mm.; yield, 78 per cent; sulfur, 21.9 and 22.1 per cent; theory, 22.5 per cent).

The general procedure comprised treatment of the sulfur compound under conditions simulating those employed in the analysis of the vulcanizates—

particularly with regard to solvents, temperatures, and reaction times.   Halo-
gen solutions in carbon tetrachloride were added to solutions of the sulfur com-
pound in a mixture of chloroform and dichlorobenzene, as in the case of the
rubber analyses.   The halogen concentration was adjusted to simulate the
rubber system after consumption of halogen by double bonds—that is, $0.08 N$
instead of $0.2 N$ halogen was employed.   Changes in concentration of this
order were found to have little effect on the reactions of the simple sulfur
compounds.

Changes in the initial ratio of sulfur compound to halogen were found to
have only slight effects on the extent of reaction, provided the ratio was kept
below about 0.2–0.3.   However, for the present considerations, only low ratios
are significant since, even for the fully cured 8 per cent sulfur stock, the ratio
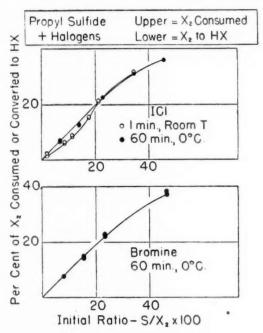
Fig. 13.—Propyl sulfide and halogens.

of sulfur to halogen (after allowing for complete saturation of double bonds)
is only about 0.25 (0.1-gram sample).

The data are plotted to show the percentage of halogen consumed and the
percentage reduced to acid by the sulfur compound as functions of the initial
mole ratios of sulfur to halogen.

Alkyl Sulfides.—In general, the reaction of iodine chloride or of bromine
appears to proceed in the manner described in the literature[10].   The halogen
addition product formed on mixing the two reactants is subsequently hydro-
lyzed (presumably forming a sulfoxide) with liberation of two moles of halogen
acid.   This is illustrated in Figure 13; either iodine or bromine reacts almost
quantitatively with propyl sulfide in the manner expected.   More drastic condi-
tions were found to cause a higher consumption of halogen together with the pro-

duction of more HX; this indicates appreciable substitution in the molecule in addition to quantitative oxidation of the sulfur; corrections for substitution in such cases gave values of almost exactly 2HX per sulfur atom. Dodecyl sulfide was found to react both additively and substitutively with iodine chloride, but chiefly by addition in the case of bromine (Figure 14); in either case, substantial proportions of acid are formed.

Propyl Disulfide.—The reaction of the halogens with propyl disulfide is shown in Figure 15.   Bromine reacts to a considerably lesser extent than iodine chloride, and apparently by substitution.   However, the reaction in one minute with iodine chloride is very small, in contrast to rubber vulcanizates which were shown to produce about one molecule of HX per sulfur atom in 1-minute reaction time.
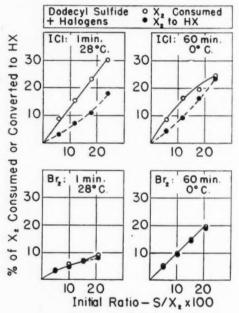
FIG. 14.—Dodecyl sulfide and halogens.

The temperature of the reaction has little effect, as evidenced in the comparison of curves for 60 minutes at 0° C and at room temperature, respectively; this suggests that the principal reaction may occur after the addition of water to the system.   The reaction of iodine chloride in the presence of large contrations of alcohol was found to give acid in excess of complete reduction of the halogen; this suggests oxidative cleavage of the disulfide to produce the sulfonic acid.

Allyl Sulfide.—Judging from halogen consumption, the reaction of allyl sulfide with the halogens (Figure 16) appears to take place principally at double bonds, with subsequent formation of halogen acid through loss of HX, although some of the HX appears to originate from substitution at the higher reaction temperature.   This behavior is similar to that of the rubber-sulfur vulcanizates, except for the lack of contrast between iodine chloride and bromine.
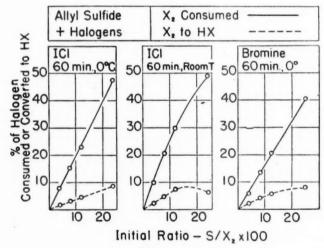
Fig. 15.—Propyl disulfide and halogens.

Fig. 16.—Allyl sulfide and halogens.

Methallyl Sulfide.—The reaction of methallyl sulfide (Figures 17 and 18) is similar to that of allyl sulfide except that formation of hydrogen bromide is negligible in the reaction of bromine with methallyl sulfide. Iodine chloride saturates both double bonds with extreme ease (almost completely in 1 minute)
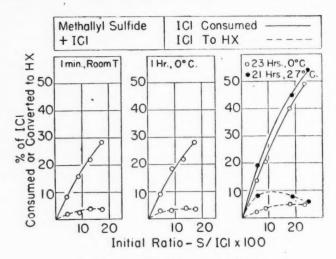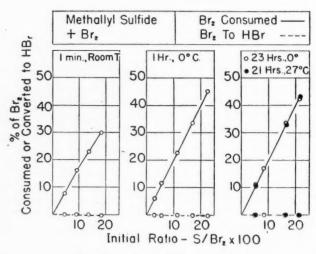

Fig. 17.—Methallyl sulfide and iodine chloride.

Fig. 18.—Methallyl sulfide and bromine.

and apparently reacts extensively by substitution under more drastic conditions. Bromine, on the other hand, appears to react exclusively to saturate the two double bonds. The acid-producing tendency is suggestive of the vulcanizates, although the acid production with iodine chloride is much less than would be anticipated, particularly under the drastic conditions.

Butylmethallyl Sulfide.—The action of the halogens on butylmethallyl sulfide is shown in Figures 19 and 20. Even under mild conditions, the reaction of iodine chloride, at low sulfur-to-halogen ratios, gives between one and two moles of HX per sulfur atom. At the same time the consumption of
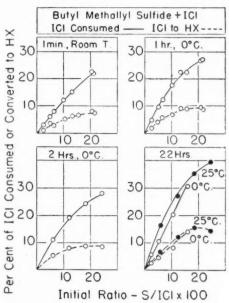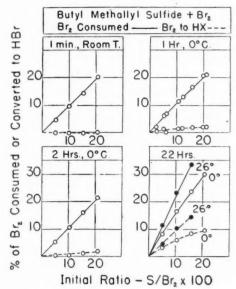

FIG. 19.—Butylmethallyl sulfide and iodine chloride.

FIG. 20.—Butylmethallyl sulfide and bromine.

halogen is considerably in excess of the amount required to saturate the double bond. Presumably one molecule of halogen is consumed in saturating the double bond—at least for reaction times in excess of one minute. If this be the case, the high acid production cannot all arise from substitution but must come in substantial proportion from either loss of HX from the double bond addition product, or partial oxidation of the sulfur to sulfoxide—more likely the former, since bromine has been shown to be at least equally effective in comparison with iodine chloride in oxidizing alkyl sulfide to sulfoxide.

Except during the long reaction times, bromine reacts almost exclusively at the double bond, since very little acid is produced. This is in agreement with the behavior of rubber-sulfur vulcanizates and bromine, where 2-hour reaction at 0° C shows virtually no increase in hydrogen bromide with increasing combined sulfur. Only with very long reaction times is appreciable hydrogen bromide produced.

CONCLUSIONS

The contrasting behavior of the methallyl sulfides with the two different halogens is analogous to that observed in the case of the pale crepe–sulfur vulcanizates. Thus, with iodine chloride in large excess, acid production reaches substantial proportions, whereas with bromine it remains negligible or very small except under most drastic time and temperature conditions. The alkylmethallyl type gives more acid with iodine chloride under mild conditions than does the dimethallyl derivative and, in this respect, resembles more closely the vulcanizates. Moreover, the alkylmethallyl structure is consistent with the loss of one double bond per sulfur atom combined, whereas the dimethallyl structure is not.

None of the other sulfur compounds studied resemble the vulcanizates. Thus, alkyl sulfides oxidize readily to sulfoxide and undergo considerable substitution, giving large proportions of acid with either iodine chloride or bromine; this type of behavior is inconsistent with the selective introduction of chlorine in proportion to HX as well as with the inactivity of bromine toward vulcanizate sulfur. Allyl sulfide is in some respects similar to methallyl sulfide, but fails to show the marked contrast between the two different halogens; this structure would, of course, not be expected of natural rubber, nor is it consistent with the loss of one double bond per sulfur atom. Propyl disulfide shows greater dependence on reaction time and less dependence on temperature than are exhibited by the vulcanizates; moreover, this structure cannot be reconciled with the loss of one double bond per sulfur atom.

Evidence favoring the alkylmethallyl sulfide linkage as typical of rubber vulcanized by sulfur only is summarized in Table III. This type of linkage is

TABLE III
EVIDENCE FOR AND AGAINST VARIOUS TYPES OF SULFUR
LINKAGES IN RUBBER-SULFUR VULCANIZATE

Possible types*	RSR	RSSR	$\overset{\text{C}}{\underset{|}{(C=C-C)_2S}}$	$\overset{\text{C}}{\underset{|}{C=C-CSR}}$
Conditions satisfied				
α-Methylenic attack	No	No	Yes	Yes
One double bond loss per sulfur atom combined	No†	No	No	Yes
Contrasting behavior toward bromine and iodine chloride	No	Yes	Yes	Yes

* R = alkyl radical.
† Unless formed by direct addition of sulfur at double bond.

the only one of those studied which satisfies all three of the criteria exemplified by the vulcanizate—namely, it can be produced by α-methylenic attack, (2) the vulcanization is accompanied by the loss of a double bond per sulfur atom, and (3) the linkage shows a characteristic reactivity toward iodine chloride in contrast to little or no reactivity toward bromine.

The most plausible mechanism of the vulcanization of rubber with sulfur alone would appear to be embodied in suggestions of Armstrong, Little, and Doak[3]. The writers' interpretation, in the light of the present work, would comprise a primary attack by sulfur at the α-methylene to form an allylic type of thiol or RS radical, followed by the addition, either intra- or intermolecularly, of the thiol to a double bond. An occasional intermolecular addition would account for the cross-bonding necessary to produce the characteristic physical properties of vulcanization. The intramolecular additions would probably produce rings of the thiophane type in agreement with the data of Midgley, Henne, and Shepard[22]. Thus, there would be produced alkylallyl thioethers of the following types:

I. Intramolecular   II. Intermolecular

Structures I and II are among those suggested on the basis of molecular model studies by van Amerongen and Houwink[23]. The proposed mechanism is consistent with both the ratio of one double bond loss per sulfur atom combined in vulcanization, and the behavior of the vulcanizates with halogens.

SUMMARY

1. When iodine chloride is used for the determination of double bonds in sulfur-vulcanized rubber or GR-S, it undergoes side reactions induced by combined sulfur.

2. Bromine in carbon tetrachloride is believed to give a satisfactory measure of the double bonds in a rubber-sulfur vulcanizate dissolved in dichlorobenzene-chloroform mixture.

3. The relation of one double bond consumed per sulfur atom combined in the rubber-sulfur type vulcanizate was confirmed.

4. Organic accelerators (in the absence of metal activators) catalyze the combination of sulfur without altering the ratio of one double bond loss per sulfur atom combined.

5. The introduction of a metal oxide or soap, such as zinc, causes a different type of vulcanization, which results in less than one double bond consumed per sulfur atom combined.

6. The reactions of propyl sulfide, dodecyl sulfide, propyl disulfide, allyl sulfide, methallyl sulfide, and butylmethallyl sulfide with iodine chloride and with bromine, respectively, are described.

7. The behavior of rubber-sulfur vulcanizates resembles that of butyl-methallyl sulfide in reactions with iodine chloride and bromine, respectively; this suggests an alkyl-allyl type sulfur bond.

8. The theory of vulcanization proposed by Armstrong, Little, and Doak, based on the α-methylenic concept of Farmer, is supported by the findings of this investigation.

ACKNOWLEDGMENT

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MINERAL SULFIDE AS INDEX OF DISULFIDE CROSS-BONDING*

C. M. Hull, S. R. Olsen, and Wesley G. France

The first paper of this series[2] confirmed that simple rubber-sulfur vulcanizates are produced with the coincident loss of a double bond per sulfur atom combined, and evidence was presented in support of a thioether linkage of the alkylallyl type. It was shown that organic accelerators may catalyze the reaction in the absence of metal oxides or salts without essentially altering the reaction.

Metal oxide– or metal soap–promoted vulcanizations, on the other hand, were shown to occur with relatively small loss of unsaturation, in agreement with the conclusions of Brown and Hauser[2] with respect to "accelerated" vulcanizations. Moreover, the metal-activated vulcanizates are characterized by greater stiffness—that is, higher elastic modulus. Until recently no satisfactory mechanism had been proposed for the action of metals in vulcanization other than the activating effect of the oxide or soap on the organic accelerator, although attempts had been made to explain the significance of mineral sulfide formation[3] accompanying vulcanization.

Armstrong, Little, and Doak[4] recently showed that a metal such as zinc enters directly into the reactions which produce cross-bonds and that the extent to which it does so, at least under certain circumstances, can be followed as a function of the metallic sulfide produced in the cure. Presenting evidence for the α-methylenic attack by sulfur as proposed by Farmer[5], these investigators suggested a mechanism of vulcanization proceeding through the formation of a substituted sulfhydryl group, which subsequently could saturate a double bond to form a thioether[1] or react with the metal to form a mercaptide. It was proposed that the mercaptide might conceivably form a cross-link with simultaneous production of a molecule of metallic sulfide in one or both of two ways: spontaneous decomposition forming a thioether, or oxidation by sulfur forming a disulfide. Thus:

$$RSZnSR \rightarrow RSR + ZnS \qquad (1)$$

$$RSZnSR + S \rightarrow RSSR + ZnS \qquad (2)$$

Since, in either case, zinc sulfide would serve to indicate the extent of cross-linking, it was believed by the writers that a further investigation of mineral sulfide formation in rubber and related systems would be of value. The present paper describes such an investigation.

ANALYTICAL PROCEDURE

A rapid method was devised for mineral sulfide based on that of Stevens[6], with two principal modifications—the use of an absorbent similar to that used by Guppy[7] and the general procedure for titration of hydrogen sulfide used by

Luke[8]. Briefly, the method consists of treating the vulcanizate or other type of sample in an inert atmosphere (carbon dioxide) with a mixture of ether and concentrated hydrochloric acid, collecting the hydrogen sulfide evolved in a buffered (sodium acetate–acetic acid) solution of cadmium chloride, and finally determining the hydrogen sulfide by titration with iodine (iodate-iodide) in acid solution. Tests with vulcanizates containing zinc sulfide in known amounts resulted in a uniform recovery of 95 per cent or more of the sulfide sulfur.

STUDY OF NONPOLYPRENE SYSTEMS

Reaction of Thiols, Sulfur, and Zinc Soap in Zylene Solution.—If vulcanization proceeds through an intermediate mercaptide as indicated above, then simple thiols, in the presence of zinc soaps and sulfur, should undergo reactions 1 or 2.

As a preliminary experiment, a mixture of 80 parts xylene, 16.8 parts dodecanethiol (93 per cent thiol), 7 parts Laurex (zinc laurate), 5 parts zinc oxide, and 1 part M.B.T. (mercaptobenzothiazole) was prepared to simulate a rubber system. After 30, 90, and 270 minutes of refluxing at 141–142° C, the mixture was tested for mineral sulfide by the hydrochloric acid–ether treatment; only a trace of hydrogen sulfide (0.04 per cent of hydrogen sulfide-producing sulfur on total mixture) was obtained. On cooling, the mixture formed a fairly stiff gel. Sulfur (3 parts) was added to the gel and the heating continued for 2 hours. After standing overnight the mixture settled into a clear, yellowish brown solution and a whitish precipitate. A portion of the solution was centrifuged to remove traces of suspended pigment, and left a perfectly clear solution. Analysis of the solution gave a zinc sulfide content accounting for 0.98 part of sulfur, or about one third of the sulfur added. Since the formation of zinc sulfide is negligible in the absence of free sulfur, the principal reaction evidently comprises the oxidation of mercaptan to disulfide as in reaction 2. Accordingly, about 80 per cent of the thiol should have been oxidized.

To avoid the inconvenience of a two-phase reaction system, further experiments in xylene were carried out in the absence of zinc oxide. Experiments were conducted in 25 cc. of xylene with varying amounts of mercaptan, sulfur, and Laurex—for example, up to 0.3 gram of sulfur and up to 3 grams of Laurex. Solutions were heated just below boiling (that is, at about 140° C). The following observations show the effects of varying the proportions of the reactants. (1) In the absence of zinc soap, the reaction (as indicated by hydrogen sulfide evolution) is practically negligible. (2) When a trace of zinc soap (Laurex) is added to the hot solution of dodecanethiol and sulfur in xylene, a copious evolution of hydrogen sulfide immediately ensues, and the solution gradually becomes turbid. Similar behavior is characteristic of any mixture of reactants which is deficient in zinc. (3) As the initial amount of zinc in the system is increased, the evolution of hydrogen sulfide decreases, and the reaction products become increasingly soluble in the system. (4) When a substantial excess of zinc soap (that is, $ZnA_2 > 2RSH$) is used, the product emerges as a clear solution containing mineral sulfide in approximate equivalence to the thiol or to the sulfur, depending on which reactant is employed in limiting amount. Evolution of hydrogen sulfide during the reaction is slight.

The results of experiments with varying amounts of the three reactants in xylene are summarized in Table I. The reaction products of the experiments in which excess zinc was used were conveniently handled as a single phase,

TABLE I

REACTION OF DODECANETHIOL, SULFUR, AND ZINC LAURATE IN
XYLENE SOLUTION (25 CC. OF XYLENE)

| Expt. No. | Reactants (grams) | | | Equivalent ratio of reactants and zinc sulfide | | | ZnS (by analysis) | | |
	Thiol*	Sulfur	Laurex	2 RSH	S	ZnA$_2$	Sol.	Insoluble	Total
				Excess Zinc Present					
1	2.00	0.203	3.00	1.00	1.4	1.4	..	..	0.90
2	1.22	0.140	3.00	1.00	1.6	2.4	..	..-	0.84
3	2.00	0.310	3.00	1.00	2.1	1.4	..	..	0.96
4	0.546	0.140	3.00	2.1	1.00	3.0	..	..	0.96
5	2.12	0.101	3.00	1.5	1.00	2.0	..	..	1.04
				Limiting Zinc Present					
6	2.02	0.140	0.259	8.3	7.8	1.00	0.01	0.89	0.90
7	2.01	0.140	0.502	4.3	4.1	1.00	0.04	0.95	0.99
8	2.01	0.140	1.001	2.1	2.0	1.00	0.35	0.65	1.00
9	2.03	0.140	2.043	1.06	1.00	1.00	0.77	..	0.77

* Analyzed 93 per cent dodecanethiol.

although some separation of excess soap as a gel usually occurred when the solutions were permitted to stand at room temperature. Tests on clear solutions, obtained by centrifuging the reaction mixture after 1-month standing, showed that all of the zinc sulfide remained unchanged in the solution phase. The products obtained in the experiments with limiting proportions of zinc, on the other hand, were treated as two distinct phases, a precipitate and a clear solution, separated by the centrifuge; mineral sulfide appeared in both phases and became increasingly evident in the solution phase as the zinc approached equivalence to the thiol. The time of reaction was prolonged to about 10 hours in the experiments with limiting zinc to observe the evolution of hydrogen sulfide; this was strong at first, subsided gradually, but remained appreciable after 6 hours. Tests with excess zinc were limited to about 1 hour; this period is sufficient for substantially quantitative oxidation of the thiol by sulfur or reduction of the sulfur by thiol, depending on which of the two reactants is in excess.

It is evident from these experiments that a thiol would be readily oxidized under vulcanizing conditions by the combined action of sulfur and zinc soap, both of which are required for the oxidation to take place. Zinc soap is observed to act in a catalytic capacity, presumably through the intermediate of a mercaptide. The presence of excess zinc soap and sulfur is effective in promoting a fairly rapid, substantially complete oxidation; the resulting byproduct is a hydrocarbon-soluble form of inorganic sulfide. The primary reaction product is presumed to be a disulfide because of the good agreement between the observed mineral sulfide and the predicted value based on the disulfide-producing reaction.

The soluble nature of the zinc sulfide produced in these experiments is undoubtedly similar to that observed previously in rubber systems[9]. In the course of the present investigation it was found that large proportions of zinc (for example, up to 5 parts or more of zinc oxide per 100 parts of rubber) can be rendered soluble as zinc sulfide; in this way a virtually clear gum vulcanizate can be produced. Analyses of clear solutions of such vulcanizates (obtained by centrifuging a solution prepared in dichlorobenzene and diluted with chloroform), for both soluble zinc and inorganic sulfide sulfur, establish the stoichio-

metric ratio required by the formula ZnS. It appears that the solubilization of zinc sulfide is effected in some manner by excess zinc soap, possibly through stabilization of a colloidal dispersion.

Reaction of Olefins, Sulfur, and Zinc Soap.—Armstrong, Little, and Doak[4] isolated allyl-type sulfides, disulfides, and polysulfides as final products in the reaction between selected olefins, sulfur, and other vulcanizing ingredients. On the basis of their results, together with the indications of the thiol experiments just described, the mechanism suggested by Armstrong, Little, and Doak, proceeding through the sequence,

$$RH \xrightarrow{S} RS- \xrightarrow{Zn} RSZnSR \xrightarrow{S} RSSR + ZnS$$

where R is an allylic radical, appears most plausible. The present authors believe that the monosulfides found by these investigators might have arisen from the mercapto-addition to double bonds. Polysulfides, on the other hand, might be considered as logical byproducts which would tie up a certain amount of the available sulfur. Assuming the above sequence of reactions without regard for polysulfide formation, one notes that a molecule of zinc sulfide accounts for the consumption of three sulfur atoms in the formation of a disulfide; polysulfide formation would use more sulfur, so that the maximum ratio of zinc sulfide to total sulfur present would be one to three. Thus, as a rough approximation, the percentage of sulfur converted to zinc sulfide may be taken as a measure of the extent to which the overall reaction has occurred, 33 per cent indicating a quantitative reaction.

Certain of the olefin experiments were repeated with the object of following inorganic sulfide under nearly normal vulcanizing conditions as an indication of the extent of overall reaction on the basis of the assumed mechanism. The experiments were carried out in sealed tubes by heating the reactants for 2 hours at 144–145° C, with or without xylene as a solvent, and with or without M.B.T. Zinc oxide was omitted to provide a homogeneous system at the vulcanization temperature. Either zinc laurate or zinc propionate was used as a source of soluble zinc. Sulfur and zinc soap were used in theoretical ratio (3 atoms of sulfur to 1 molecule of soap) except in experiment 6 where the sulfur was doubled. The olefin was present in several-fold excess at the start of the reaction.

The results are summarized in Table II. Products from experiments 1 to 4 were centrifuged but failed to give more than a negligible residue; analysis was carried out on the centrifuged solution. Experiment 5 gave a voluminous gel from which a representative aliquot was taken for analysis. Experiment 6 gave a reddish brown mobile liquid. Experiment 7, in which zinc propionate was used as a source of soluble zinc, gave a precipitate in which substantially all of the mineral sulfide was concentrated; this is in accord with the results of Armstrong and coworkers, who used zinc propionate exclusively in their work with simple olefins.

Interpreted on the basis of the above squence of reactions, the results of Table II can be summarized as follows:

(1) The overall reaction proceeds rapidly; it reaches substantial proportions (for example, 75 per cent of theory in Experiment 1 and 84 per cent of theory in Experiment 6) under conventional vulcanization conditions.

(2) The reaction in the presence of a higher zinc soap, such as zinc laurate, produces a soluble zinc sulfide similar to that obtained from a thiol or from rub-

TABLE II

REACTION OF OLEFINS WITH SULFUR UNDER VULCANIZING CONDITIONS
(2 HOURS AT 144.5° C)

Expt. No.	1	2	3	4	5	6	7
Formula (grams)	..	..	..	Blank	..	..	..
2-Methyl-2-butene	0.700	0.716	..	..	0.744	0.763	0.717
Cyclohexene	..	..	0.877	..	..	..	..
Sulfur	0.064	0.064	0.064	0.064	0.064	0.128	0.064
Zinc laurate	0.309	0.309	0.309	0.309	0.309	0.309	..
Zinc propionate	..	..	..	..	..	..	0.141
M.B.T.	0.020	0.020	0.020	0.020	..	0.020	0.020
Xylene	..	1.755	1.610	2.520	1.700	1.800	1.601
Total grams	1.093	2.864	2.880	2.913	2.817	3.020	2.543
ZnS sulfur (grams)	0.017	0.017	0.012	0.0006	0.0042	0.019	0.013*
Percentage of S to ZnS	25	23	17	..	6	14	19
Percentage of theory†	75	69	51	..	18	84‡	57

* Found in residue, others in solution.
† Based on assumed sequence of reactions: $RH \xrightarrow{S} RS \xrightarrow{Zn} (RS)_2Zn \xrightarrow{S} RSSR + ZnS$.
‡ Based on zinc present. Zinc laurate is limiting since there is only ⅓ of a millimole present for 4 milliatoms of sulfur.

ber, whereas that in the presence of zinc propionate gives zinc sulfide as a precipitate insoluble in the system (Experiments 2 and 7).

(3) The reaction is increased to a marked degree by M.B.T., although a considerable amount of reaction occurs in 2 hours without the accelerator (Experiments 2 and 5).

(4) The tendency to undergo the reaction is apparently less in the absence of a methyl group on the olefinic carbon (for example, 2-methyl-2-butene *vs.* cyclohexene as in Experiments 2 and 3). This may be due either to less overall reaction or to relatively greater tendency to side reaction, such as mercapto-addition, in the case of cyclohexene.

MINERAL SULFIDE FORMATION IN POLYPRENE SYSTEMS

Procedure.—Typical formulas were compounded on a small laboratory mill and cured in a laboratory press at suitable temperatures, usually 141° C for rubber and 144° C for GR-S, except in a few series where effect of long curing times was observed by curing at 150° C and calculating equivalent times at 141° C. Samples were analyzed for free sulfur by the method of Oldham, Baker, and Craytor[10] and combined sulfur (S_c) was calculated by difference. Zinc sulfide sulfur (S_{ZnS}) was determined as hydrogen sulfide after treatment of the sample with hydrochloric acid–ether mixture as described. Results are all expressed in grams per 100 grams of elastomer.

Direct Action of Oxides and Soaps with Sulfur.—The question arose as to whether the various metals commonly employed in rubber vulcanization could yield the corresponding sulfide by direct reaction of the oxide or soap with sulfur in the presence of other vulcanizing ingredients; the problem was investigated by heating mixtures of these substances in Vistanex polybutylene. The formula used was Vistanex 100, stearic acid 4, sulfur 8, M.B.T. 1, and oxide equivalent to 5 parts of zinc oxide; conversion of all the metal to sulfide would yield 1.97 parts of sulfide sulfur. The mixture was heated for 2 hours at 142° C. The respective yields of sulfide sulfur from zinc, lead, and cadmium oxides, expressed as parts of sulfur per 100 parts of Vistanex, were: zinc oxide, 0.09; lead oxide 1.33; and cadmium oxide, 0.44. These results show that the forma-

tion of zinc sulfide by direct action is negligibly small; therefore, it is assumed that any metal sulfide produced in the tests with polyprenes and zinc oxide or zinc soaps arises through intermediate reaction of the polyprene. Because of the complicating direct reaction in the case of lead or cadmium, the present considerations are limited largely to the reactions of zinc, although similar reactions undoubtedly occur with the other two metals.

Effect of Zinc Solubility.—The need for solubilizing zinc oxide to utilize its desirable effects in vulcanization was first demonstrated by Russell[11], who showed that rubbers deficient in natural fat acid failed to respond properly to the toughening effect of zinc oxide. Whitby and Evans[12] showed that certain accelerators, especially M.B.T., are more dependent on fat acid than others— for example, D.P.G. (diphenylguanidine). Russell later[13] demonstrated conditions under which zinc oxide may be rendered soluble in a hydrocarbon medium. The effect of organic bases in promoting solution is striking, and explains the smaller dependence of an accelerator like D.P.G. on added fat acid.

Brazier and Ridgway[14] found that D.P.G. stocks developed a particularly large amount of zinc sulfide, but that the addition of oleic acid caused no significant change. These results are in accord with the observations of Russell relative to the peculiar solubilizing action of organic bases, if it be assumed that the amount of zinc sulfide produced is a function of the concentration of soluble zinc. These investigators showed further that the presence of small amounts of magnesia inhibits the zinc sulfide–producing reaction in the case of D.P.G. vulcanizates.

It was found in the present investigation that the solubilization of zinc oxide or the use of zinc soaps enhances the formation of zinc sulfide and, at the same time, develops stiffer vulcanizates in accord with the postulated reactions of vulcanization. It was shown further that magnesia has a general inhibiting action on zinc sulfide formation and also suppresses modulus development.
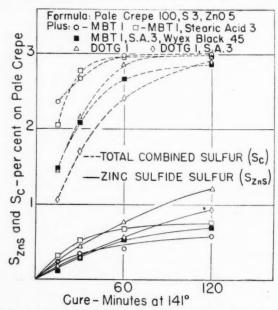

Fig. 1.—Rate of sulfur combination and zinc sulfide formation in typical rubber stocks.

Curves showing the rate of combination of sulfur and the rate of formation of zinc sulfide in a few typical natural rubber stocks are shown in Figure 1. Curves showing zinc sulfide as a function of total combined sulfur are shown in Figure 2. The marked tendency of the D.O.T.G. (di-*o*-tolylguanidine) stock to develop zinc sulfide is believed by the authors to be associated with its ability to solubilize zinc oxide; this property also contributes to higher modulus in this type of-vulcanizate, as will be discussed later; the limit of about 1.21 per cent inorganic sulfide sulfur was not increased by extending the cure to 216 minutes at 150° C. The addition of stearic acid to the M.B.T. stock results in a marked enhancement of zinc sulfide formation and gives a stiffer vulcanizate, whereas
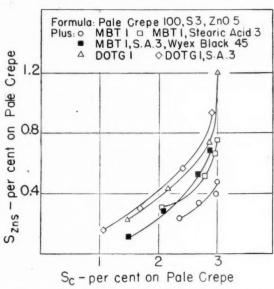
Fig. 2.—Zinc sulfide as a function of total combined sulfur in typical rubber stocks.

the addition of a similar amount of stearic acid to the D.O.T.G. formula retards both total sulfur and zinc sulfide combination, effecting no substantial change in the ratio of zinc sulfide to total combined sulfur. Carbon black retards the cure of the M.B.T. stock but has little effect on the ratio of zinc sulfide to total sulfur.

The increasingly greater slopes of the curves of Figure 2 with increasing combination of sulfur, ultimately approaching the vertical, indicate the formation of zinc sulfide from sulfur previously combined in some other form; this fact was also noted by Brazier and Ridgway[14]. A polysulfide is suggested as an intermediate, in line with the proposal of Bedford and Sebrell[15] that acceleration generally proceeds through polysulfide formation. The presence of polysulfides in the reaction products of simple olefins and sulfur was established by Armstrong, Little, and Doak[4].

The effect of soluble zinc is further illustrated in Figure 3, which shows the increase in zinc sulfide production for 2-hour cures with increasing zinc laurate concentration. The curve approaches a maximum of about 1.1, which represents 37 per cent of the sulfur in the stock and checks approximately the limit of about 1.2 observed with the D.O.T.G. stock. In terms of the proposed
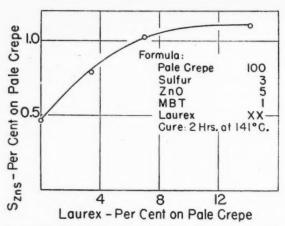
Fig. 3.—Effect of zinc laurate concentration on zinc sulfide formation.

mechanism through reaction 2, the limit of sulfur conversion represents an excess over the theoretical ($33\frac{1}{3}$ per cent). The excess could be accounted for by assuming that part of the zinc sulfide arises from side reactions.

Effect of Accelerators on Zinc Sulfide.—The formation of zinc sulfide does not depend on the presence of an accelerator when the zinc is supplied in soluble form. This is illustrated in Figure 4, which compares a given stock with and
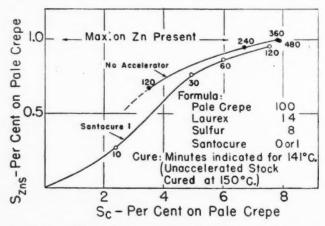
Fig. 4.—Zinc sulfide as a function of total combined sulfur in accelerated and unaccelerated high sulfur stock.

without organic acceleration. In spite of the great difference in curing rates, the two stocks show little difference with respect to the proportion of sulfur converted to zinc sulfide. However, as already indicated, certain accelerators are believed to promote the solubilization of zinc and thus lead to enhanced production of zinc sulfide. A comparison of various accelerator combinations with this viewpoint is shown below, with base stock comprising pale crepe 100,

sulfur 3, zinc oxide 5, and accelerator as indicated:

Accelerator, parts	ZnS Sulfur (2-hr. cure)
D.O.T.G. (1)	1.21
M.B.T. (1), Laurex (7)	1.11
A-808 (0.5)	1.08
Hepteen (2.5)	0.94
Santocure (1.0)	0.90
2 M.T. (0.7)	0.70
Zimate (0.6)	0.63
Monex (0.3)	0.52
M.B.T. (1.0)	0.47

The more basic types of accelerator appear at the top of the list, associated with high zinc sulfide, possibly reflecting the ability of the basic accelerators to solubilize zinc.

As would be expected, variation in concentration of an accelerator like M.B.T. causes no substantial change in the zinc sulfide production curve. This is shown in Figure 5 for base formulas with and without supplementary
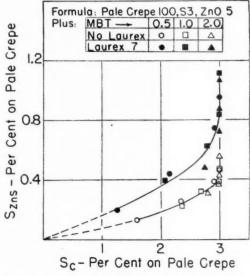
zinc in the form of laurate. The marked effect of zinc soap is again evident. The pronounced rise in zinc sulfide after the substantial disappearance of free sulfur is apparent in the Laurex stocks (cf. Figure 2, D.O.T.G. stock).

Magnesia Effect.—The suppressing action of magnesia on inorganic sulfide, first noted by Brazier and Ridgway[14] in connection with D.P.G. vulcanizates, was shown to be quite general. Furthermore, the effect is associated with a parallel diminution in modulus. The effect of magnesia on the proportion of sulfur combining as zinc sulfide is shown in Figure 6 for a D.O.T.G. stock as well as for an M.B.T. stock in the presence of added zinc soap. Magnesia was found to have a negligible effect on zinc sulfide in the M.B.T. stock which was not augmented with zinc soap (Table III, stocks 3 and 7). Furthermore,

the magnesia-containing formulas, including the D.O.T.G. formula, behave similarly to one another and to the M.B.T. stock without added zinc soap (Figures 5 and 6, lower curves).   Thus it appears that magnesia counteracts the influences which cause solubilization of zinc.   Increasing the magnesia from 1 part to 5 parts (tested only in the M.B.T.–Laurex stock) gave almost identical results.   GR-S, isoprene-styrene polymer, and acetone-extracted pale crepe respond similarly; in the case of GR-S, the presence of magnesia approximately halves the zinc sulfide.   Tread stocks behave in the same manner as gum stocks as would be expected, since carbon black has little effect on zinc
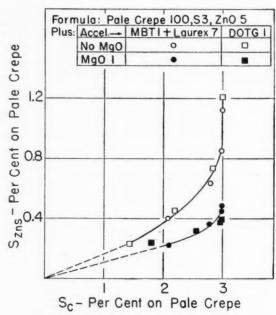

FIG. 6.—Effect of magnesia on zinc sulfide formation.

sulfide formation (Figure 2).   A variety of formulas containing different accelerators, including Monex, Santocure, Butyl Zimate, and others in addition to those cited, were all affected by magnesia in a similar fashion.   No adequate explanation of the magnesia effect can be offered at this time, although it is believed to be related to the modulus-building reactions of the sulfhydryl group. · The effect is not related to rate of curing since magnesia may accelerate or decelerate the combination of sulfur, depending on the circumstances—for example, with M.B.T. or Santocure acceleration it increases the rate of combination in GR-S, whereas it decreases the rate slightly in natural rubber.   With D.O.T.G. acceleration, on the other hand, magnesia increases the rate of sulfur combination in natural rubber.

   Comparison of Elastomers.—Figure 7 shows the relative capacities toward formation of mineral sulfide sulfur in the case of three different elastomers (natural rubber, GR-S, and isoprene-styrene copolymer containing about 80 per cent isoprene units by weight).   The greater production of mineral sulfide on the part of natural rubber and the isoprene-styrene polymer as compared to

standard (butadiene) GR-S is undoubtedly associated with the influence of the α-methyl group.   The role of the acetone extract portion of natural rubber is apparently not significant, provided sufficient soluble zinc is supplied in the form of soap; otherwise, the results with natural rubber would show greater contrast to those with the synthetic isoprene polymer.   Actually, the zinc sulfide obtained with these two elastomers is in the approximate ratio of iso-
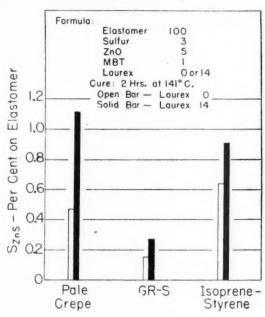

Fig. 7.—Relative tendencies of various elastomers to form zinc sulfide.

prene unit content.   The low values for zinc sulfide in the case of GR-S are probably indicative of a preference for the mercapto addition reaction in the vulcanization of this elastomer.

Relation of Zinc Sulfide to Modulus.—The relation of zinc sulfide to modulus is difficult to evaluate in a general way because a number of factors—other than the reactions proposed to account for the formation of zinc sulfide during vulcanization—undoubtedly enter into the building or destroying of cross-links and, possibly, into the formation of zinc sulfide.   Thus, extended curing of natural rubber eventually effects a complete collapse of tensile properties; oxidation in rubber, likewise, leads to breakdown.   On the other hand, the same circumstances in the case of GR-S lead to an increase in cross bonding.

In some vulcanizates, however, such as those described by Armstrong, Little, and Doak, there appears to be justification for associating the modulus-building reaction with that which forms zinc sulfide.   Those investigators showed a linear relation for most of the curve of modulus against zinc sulfide in the case of an M.B.T. formulation containing substantial zinc soap with variable sulfur and curing time.   This relation was confirmed in the present investigation.   However, it was found that a change in accelerator concentration produces a family of curves whose slopes increase as the accelerator con-

centration is increased (Figure 8).   Thus, the net effect of higher accelerator concentration appears to be greater efficiency of cross-linking corresponding to a given zinc sulfide production; this may result from minimized degradation reactions because of the reduced time of vulcanization with higher accelerator concentration.

The relation between modulus and zinc sulfide demonstrated by Armstrong and his coworkers fails in the absence of added zinc soap or in the presence of soap and magnesia, and the cure undergoes drastic reversion (Figures 8 and 9) Complete curing and analytical data for these stocks are given in Table III.
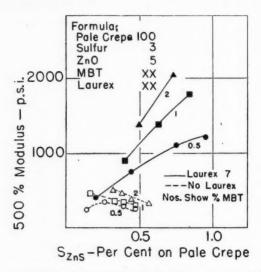

FIG. 8.—Effect of accelerator concentration and of added Laurex on relation of zinc sulfide to modulus in M.B.T. stocks.
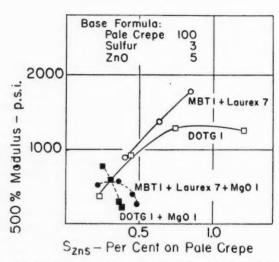

FIG. 9.—Effect of magnesia on relation of zinc sulfide to modulus.

TABLE III

COMPLETE CURING AND TEST DATA ON STOCKS OF FIGURES 9 AND 10

(General formula: pale crepe 100, sulfur 3, zinc oxide 5)

Expt. No.	Stock composition	Cure (min. at 141° C)	S_c (% on pale crepe)	S_{ZnS} (% on pale crepe)	M-300 (lbs. per sq. in.)	M-500 (lbs. per sq. in.)	Tensile strength (lbs. per sq. in.)	Elonga-tion (%)
1	M.B.T. 0.5	15	1.60	0.14	110	255	1790	800
		30	2.34	0.26	130	340	1980	775
		60	2.91	0.39	135	290	2180	850
		120	2.99	0.47	115	250	1870	850
2	M.B.T. 0.5 + Zn laurate 7	15	1.27	0.20	150	400	2060	750
		30	2.15	0.44	250	750	3340	700
		60	2.92	0.75	280	1100	2800	685
		120	2.99	0.95	300	1210	2160	575
3	M.B.T. 1	15	2.36	0.23	180	460	2740	775
		30	2.68	0.33	160	360	2780	815
		60	2.98	0.39	145	340	1320	760
		120	2.99	0.47	110	290	1210	735
4	M.B.T. 1 + Zn laurate 7	15	2.08	0.40	230	900	4100	725
		30	2.79	0.63	350	1380	3080	700
		60	2.98	0.84	380	1780	2460	535
		120	2.99	1.11	..	..	..	..
5	M.B.T. 2	15	2.79	0.32	190	530	2950	760
		30	2.98	0.38	170	485	2860	800
		60	2.99	0.44	155	385	2400	775
		120	2.99	0.56	145	340	2000	800
6	M.B.T. 2 + Zn laurate 7	15	2.75	0.49	340	1400	3900	650
		30	2.98	0.73	430	2050	2500	625
		60	2.99	0.88	440	..	440	300
		120	2.99	1.07	..	..	325	250
7	M.B.T. 1 + MgO 1	15	2.01	0.18	160	465	2370	750
		30	2.60	0.28	155	410	2220	775
		60	2.94	0.35	155	365	2450	800
		120	2.99	0.40	125	260	2000	950
8	M.B.T. 1 + Zn laurate 7 + MgO 1	15	2.09	0.22	180	530	4500+	800
		30	2.77	0.36	180	580	3160	760
		60	2.98	0.45	160	410	2100	750
		120	2.99	0.48	115	270	1680	770
9	D.O.T.G. 1	15	1.47	0.23	115	385	2220	750
		30	2.16	0.44	215	930	3600	675
		60	2.86	0.74	260	1290	4500+	650
		120	2.99	1.21	270	1260	3200	625
10	D.O.T.G. 1 + MgO 1	15	1.82	0.25	175	780	4500+*	750
		30	2.54	0.31	180	600	3300	735
		60	2.97	0.36	130	310	2640	800
		120	2.98	0.38	85	230	2100	850

* Capacity load for Scott tester.

Although the added zinc soap causes a slight retardation in combination of sulfur, it effects a pronounced enhancement of zinc sulfide and modulus. Magnesia counteracts the effect of the added zinc soap in the M.B.T. stock both with respect to zinc sulfide and modulus. The uninhibited D.O.T.G. vulcani-

zates in the early stages of cure follow closely on the path of the M.B.T. stock with added zinc soap.   Magnesia accelerates physical cure at the start but causes rapid reversion with continued curing, together with diminution of zinc sulfide.

The relatively small tendency of GR-S vulcanizates to form zinc sulfide, and the known tendency of GR-S to stiffen due to causes unrelated to zinc sulfide formation, make the relation between zinc sulfide and modulus of somewhat questionable significance.   However, there is a general trend of increasing modulus with increasing zinc sulfide in these stocks (Figure 10).
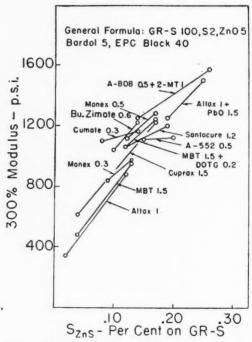
Fig. 10.—Relation of zinc sulfide to modulus in GR-S tread stocks.

Attempts to enhance zinc sulfide in GR-S vulcanizates by using soluble zinc and solubilizing agencies in a variety of forms, and by employing various active accelerating combinations, met with little success.   It is believed, therefore, that GR-S vulcanization has a decided preference for the mercapto addition reaction[1], and that a greater percentage of intermolecular additions occur than in the case of natural rubber.   Thus, in metal-activated cures, natural rubber vulcanizates may be cross-linked principally through disulfide bonds with an occasional thioether cross-link, whereas GR-S vulcanizates may be linked chiefly by thioether bonds with an occasional disulfide link.

CONCLUSIONS

The present studies of inorganic sulfide in vulcanizate and similar systems support the mercapto-mercaptide-disulfide course of reaction.   The results leave little doubt that mercaptides formed during vulcanization would sub-

squently undergo oxidation by sulfur in preference to thermal decomposition. Presumably the mercaptide reaction proceeds simultaneously with the addition of sulfhydryl groups to double bonds[1], so that the nature of the vulcanizate depends on the relative dominance of these competing reactions.

SUMMARY

1. The mechanism proposed by Armstrong, Little, and Doak to explain sulfur vulcanization in the presence of metal soap was investigated in polyprene and simpler systems from the viewpoint of the inorganic sulfide produced and, in the case of polyprenes, of the accompanying modulus.

2. Dodecanethiol was found to react with sulfur and zinc soap to produce inorganic sulfide equivalent to the oxidation of 80 to 100 per cent of the thiol to disulfide; with excess thiol substantially quantitative conversion of sulfur or of zinc soap to inorganic sulfide can be obtained.

3. Several simple olefins were found to react readily with sulfur and zinc soap under vulcanizing conditions. The reaction is promoted by M.B.T. On the basis of the mechanism assumed, the inorganic sulfide formed is sufficient to indicate extensive conversion of the olefin to a substituted diallyl disulfide.

4. Assuming the validity of the proposed mechanism, inorganic sulfide production indicates substantial disulfide cross-linking between α-carbon atoms in conventional cures with natural rubber, and appreciable, though relatively less, cross-bonding of this type in the case of GR-S. The smaller extent of this type of cross-linking with GR-S is believed to result from greater tendency on the part of this elastomer to add the intermediate mercapto compound to double bonds, as proposed in the first paper of this series.

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CHEMICAL DERIVATIVES OF SYNTHETIC ISOPRENE RUBBERS*

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Natural rubber was the subject of intensive investigation with respect to its chemical reactions and the preparation of commercially useful derivatives. General reviews in this field have been written by Fisher[1], Schidrowitz[2], Jones[3], Sibley[4], Memmler[5], Dawson and Schidrowitz[6], and Farmer[7]. Before World War II several of these reaction products, such as rubber hydrochloride (Pliofilm), isomerized rubber (Pliolite), and chlorinated rubber (Parlon), had been marketed successfully.

During the past five years drastic restriction of the commercial use of natural rubber for chemical derivatives prompted the study of synthetic rubbers for this purpose. Endres[8] recently reported on chlorinated and cyclized synthetic rubbers, with special emphasis on GR-S as the starting material.

This paper deals particularly with derivatives of polyisoprene and other isoprene-containing synthetic rubbers which behave chemically very much like natural rubber because of the similarity in structure. It is shown that GR-S and other butadiene-containing synthetic rubbers, under the same conditions, are either nonreactive or behave differently.

Because of its similarity to the natural rubber product, isomerized synthetic polyisoprene has been designated Pliolite S-1. Chlorinated synthetic polyisoprene is referred to as Pliochlor.

CYCLIZED IOSPRENE POLYMERS

The formation of rubber isomers by reaction with halides of amphoteric metals, such as stannous and stannic chlorides, aluminum chloride, boron fluoride, and chlorostannic acid, was reported by Bruson, Sebrell, and Calvert[9]. The properties of such derivatives which render them useful as molding materials were described by Thies and Clifford[10] and by Jones and Winkelmann[11]. Properties of Pliolite-rubber mixtures were described by Thies[12]. Thermoprenes, which are reaction products of rubber and sulfuric acid or sulfonic acids, were investigated by Fisher and co-workers[13], who considered them to be cyclic isomers of the rubber hydrocarbon. Endres[8] described the cyclization of GR-S at 160–180° C with stannic chloride in phenol, cresol, naphthalene, etc. Buizov and Kusov[14] studied the preparation of thermoprenes from sodium-butadiene rubber and found that, compared to natural rubber, they were relatively inert. The difference was attributed to lack of side chains.

CYCLIZATION OF POLYISOPRENE

Synthetic isoprene polymers, such as polyisoprene and copolymers of isoprene with styrene and other monomers, were found to react with isomerizing

agents such as stannic chloride and boron fluoride in a manner similar to that of natural rubber. The following laboratory preparation of Pliolite S-1 is typical.

Eighty grams of polyisoprene were dissolved in 675 cc. of benzene to make a 12 per cent solution, the initial viscosity of which was 37 r.p.m. on the Stormer viscometer (100-gram weight). The solution was placed in a 2-liter, three-necked flask equipped with a stirrer, thermometer, and reflex condenser and was heated in a water bath to 75° C. Then 8 per cent stannic chloride (calculated on the polyisoprene) dissolved in 50 cc. of benzene was added, half at once and the remainder 5 minutes later. The solution thickened and gelled, but within 10 minutes it was much thinner than it was originally. The reaction temperature was maintained at 70–75° for 90 minutes. The catalyst was then destroyed by the addition of 77 cc. of water and 5-minute additional stirring. The final Stormer viscosity (100-gram weight) was 715 r.p.m.

To isolate the product, the solution was mixed with 2 volumes of water, and steam was passed through the emulsion with vigorous agitation until the solvent was completely removed. Excess acidity was neutralized with dilute caustic solution. The product was separated and washed repeatedly with warm water, then vacuum-dried at 75° C for 8 hours. It had a heat distortion point of 65° C.

The type of antioxidant used to protect polyisoprene was found to have considerable effect on the color of the isomerized product. If phenyl-β-naphthylamine is used, the product is cream-colored and its solutions are brown. If a nondiscoloring antioxidant is used, the rubber and resulting cyclized product are considerably lighter in color. It is believed that at least some of the antioxidant passes unchanged through the isomerization process and is still available to protect the product against oxidation, as evidenced by the fact that antioxidant-free rubber gives an insoluble, cyclized product.

The plasticity of the original polyisoprene and the initial solution viscosity apparently have little effect on the heat distortion point of the cyclized product if sufficient time is given for complete reaction.

The actual isomerization process of polyisoprene was found to be almost identical with natural rubber with respect to solvent, reaction time, reaction temperature, and amount of catalyst required to obtain a resin of the same heat distortion point. It is desirable, however, to start with a lower solution viscosity and react to a lower viscosity than was the practice with natural rubber. Comparison of initial and final solution viscosity shows the same enormous decrease as is found with natural rubber[12].

When stannic chloride is used, the final product has an ash content of 2–3 per cent which is largely metastannic acid or stannic oxide formed by hydrolysis of the catalyst. The use of boron fluoride (either as the gas or the ether complex) results in a lower ash product because its hydrolysis products are water soluble. Polyisoprene can also be isomerized to a resin with hydrogen fluoride, a catalyst employed by Lawson[15], Garvey[16], and Söll and Koch[17] on natural rubber. Under the same conditions GR-S remains unaffected.

To obtain isomerized polyisoprene with heat distortion point of 55–65° C, 7.5 per cent stannic chloride or 10 per cent boron fluoride-ether complex is required. On a molar basis this represents 1 mole of stannic chloride for twenty-five $C_{10}H_{16}$ units, or 1 mole boron fluoride for ten $C_{10}H_{16}$ units. Apparently stannic chloride is a more efficient catalyst than boron fluoride (as the ether complex) for polyisoprene reaction.

PROPERTIES OF PLIOLITE AND PLIOLITE S–1

Table I lists a number of properties of Pliolite and Pliolite S-1, comparing unmilled resin with resin hot-milled for 5 minutes. The chief effect of milling is to make the resin more soluble and to give lower viscosity solutions. The two products are comparable in specific gravity, index of refraction, ash, iodine number, chlorine content, and per cent acetic acid formed by chromic acid

TABLE I

PROPERTIES OF PLIOLITE AND PLIOLITE S-1

| | Pliolite S-1 | | Pliolite | |
	Unmilled	Milled	Unmilled	Milled
Color	cream	brown	cream	amber
Specific gravity	1.09	1.04	1.12	1.06
Refractive index	. .	1.535	. .	1.545
Ash (%)	2.12	1.89	1.70	1.69
Iodine	157	163	180	180
Chlorine (%)	1.52	1.28	1.01	1.63
Intrinsic viscosity	0.36	0.25	0.49	0.41
Gel (%)	0	0	0	0
Heat distortion point (° C)	. .	62	. .	54
Acetic acid (chromic acid oxidation) (%)	28.3	24.9	29.7	24.1
Solution viscosity (Ford cup No. 4) (min.)				
Toluene, 10%	0.21	0.18	0.26	0.21
20%	0.62	0.25	2.13	0.64
30%	3.46	0.58	15.75	3.44
Textile spirits, 10%	0.18	0.17	0.20	0.19
20%	0.36	0.21	0.91	0.37
30%	1.87	0.35	12.97	3.31
Resin/paraffin, 30/70				
Brookfield viscosity, centipoises				
180° F	2520	2250	6775	2370
200° F	2015	870	5050	2240
235° F	965	760	1810	775
M.V.T.R. (5 lb. per ream coating), g. per 100 sq. m. per 24 hrs.	0.40	0.47	0.78	0.70
Glassine coating				
M.V.T.R. (3 lb. per ream coating)	0.32	0.21	1.33	0.19
Tinius-Olsen stiffness test				
Bending moment (in.-lb.)		1.32		5.68
Angle at break (degrees)		5		17
Water absorption (20 hrs. at 70° C) (mg. per sq. in.)	8–10		3–5	

oxidation[18]. Pliolite S-1 has a lower molecular weight, as indicated by lower intrinsic viscosity. Pliolite S-1 gives lower viscosity solutions in toluene and textile spirits; the values in the latter solvent are plotted in Figure 1. Pliolite S-1 is more brittle and weaker than Pliolite at room temperature, as measured on the Tinius-Olsen stiffness tester.

A Pliolite S-1/paraffin 30/70 mixture shows considerably lower Brookfield viscosities in the range 180–235° F than the corresponding Pliolite mixture and is therefore, more advantageous to use in hot melt dips. The moisture vapor transmission rate (M.V.T.R.) of a 5 pounds per ream coating on glassine is considerably lower than that for the Pliolite coating. A glassine coating (3 pounds per ream) containing Pliolite S-1 is much lower than that for Pliolite using unmilled resin, and about the same for milled resin. This is an advantage

for Pliolite S-1 because it could be used unmilled, whereas Pliolite would have to be milled first.   The difference can be attributed to the greater true solubility of Pliolite S-1 in the unmilled state.

The water absorption characteristics of both Pliolite and Pliolite S-1 are good.   Pliolite values are lower, probably because of the simpler method used for isolating the product.

The heat distortion point was obtained on a molded strip, $1 \times 10 \times 0.05$ inch, suspended at the ends in a water bath.   The middle of the strip was periodically deflected and held for 15 seconds at various temperatures.   The
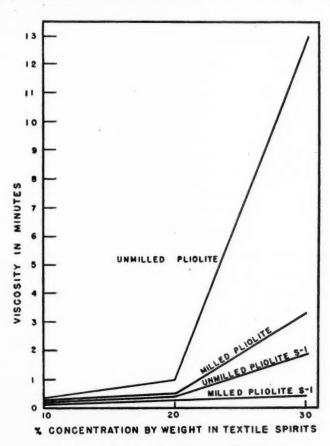
Fig. 1.—Solution viscosities of Pliolite and Pliolite S-1.

permanent set at the bow in the center was measured after relieving the pressure and removing from the water bath.   The temperature at which the bow reached 0.25 inch was the heat distortion point.

In general, Pliolite S-1 shows the same solubility characteristics as Pliolite. It is soluble in benzene, toluene, gasoline, mineral spirits, kerosene, chloroform, Troluoil, etc.   It is slightly soluble in ethyl acetate (4 per cent), methyl ethyl ketone (1.7 per cent), or acetic acid (0.7 per cent), and insoluble in dioxane,

alcohol, and acetone. Pliolite S-1 is completely compatible with mineral waxes such as paraffin and ceresin.

Pliolite S-1 has excellent electrical properties, which compare favorably with those reported for Pliolite by Thies[12]. The following data give electrical properties of Pliolite S-1/low-water-absorption GR-S, 50/50 master batch:

	1 Kilocycle	1 Megacycle
Dry sample		
Dielectric constant	2.60	2.63
Power factor (%)	0.167	0.274
Loss factor	0.0043	0.0072
D.C. specific resistivity at 540 volts (ohm-cm.)	3.6×10^{14}	3.6×10^{14}
After 24-hr. immersion in water at 50° C		
Dielectric constant	2.68	2.73
Power factor (%)	0.195	0.493
Loss factor	0.0052	0.0135
D.C. specific resistivity at 540 volts (ohm-cm.)	10.1×10^{14}	10.1×10^{14}

Pliolite and Pliolite S-1, when subjected to pyrolytic distillation under reduced pressure, behave in a similar manner, yielding 85–88 per cent of liquid distillate of the following properties:

	Pliolite S-1	Pliolite
Density (d_{22}^{22})	0.948	0.951
Refractive index (n_D^{32})	1.520	1.525
Boiling point range (740 mm., ° C)	90–340	50–330

Analysis of the distillates by boiling point, density, and refractive index showed a close correlation between the two materials.

USES OF PLIOLITE S-1

A number of applications for Pliolite S-1 were found where Pliolite was formerly used. It is an excellent reinforcement agent for natural rubber, GR-S, butyl rubber, and other synthetic rubbers. It can be used as a dispersing medium for paints, printing inks, etc. Its compatibility with waxes allows its use in hot paraffin dips. It has found use in paper coatings for glassine, kraft paper, label coatings, etc. When used in rubber-coated fabrics, improved feel, embossing characteristics, and abrasion resistance are obtained.

When Pliolite S-1 is used with many synthetic rubbers, it improves processing, decreases tack, reinforces while maintaining elongation and flexibility, maintains good electrical properties, and results in stocks of low gravity. Even a small amount of Pliolite S-1 in a rubber mix improves ease of banding on the mill. Extrusion operations are improved; the presence of Pliolite S-1 results in smoother extrusion surfaces or higher rate of extrusion. In high-gum compounds for thin-wall tubing, Pliolite S-1 imparts stiffness in the uncured state and permits perfect centering during extrusion. Calender and frictioning processability are similarly improved, since Pliolite S-1 tends to reduce lacing on the rolls.

Table II lists a number of master batches of Pliolite and Pliolite S-1 with natural rubber, GR-S, and Butyl rubber. Stress-strain values on molded, uncompounded stocks show that Pliolite reinforces natural rubber more efficiently than does Pliolite S-1, but the resins are equivalent with GR-S. The mixes in each case were prepared by banding the resin on a hot mill (200–215° F) and adding the rubber in small amounts. During mixing, the batch was cut back and forth in the usual manner until a homogeneous stock was obtained.

TABLE II

COMPARISON OF PLIOLITE AND PLIOLITE S-1 REINFORCEMENT PROPERTIES

Composition	Shore hardness (A)		Tensile* (lbs. per sq. in.)	Elongation* at yield point (%)	Shore hardness (D)
	Hot mill	Remilled cold			
Pliolite/rubber					
50/50	68	66	750	40	..
60/40	95	90	1000	10	45
70/30	95	90	1600	2	60
Pliolite S-1/rubber					
50/50	70	60	200	12	20
60/40	90	80	600	10	35
70/30	100+	90	1300	0	58
Pliolite/GR-S					
50/50	100+	75	300	10	22
60/40	100+	Too rough	850	7	38
70/30	100+	Too rough	1500	2	55
Pliolite S-1/GR-S					
50/50	100+	70	300	11	20
60/40	100+	90	1100	5	42
70/30	100+	Too rough	1400	3	52
Pliolite S-1/Butyl					
50/50	80	75	1000	250	..

* Molded 10 min. at 230° F.

The stock was given a few passes through a cold mill before molding to give a smooth, flexible stock. The reverse method of adding Pliolite S-1 to the rubber on the mill usually is not successful because the Pliolite S-1 is merely dispersed in the rubber as a pigment and gives a grainy, nonhomogeneous master batch. Pliolite S-1 master batches with a number of synthetic rubbers can be easily blended with more rubber and compounding ingredients. Figure 2 is a plot of the tensile strength of uncompounded, molded Pliolite-rubber mixtures as a function of the Pliolite content.

The incorporation of Pliolite S-1 in a GR-S gum stock increases the hardness, tensile, and elongation:

Parts Pliolite S-1	0	10	20
GR-S (Naugatuck)	100	90	80
Pliolite S-1/GR-S, 50/50	..	20	40
Sulfur	2	2	2
Zinc oxide	5	5	5
Stearic acid	1	1	1
Tetramethylthiuram monosulfide	0.50	0.50	0.50
Properties (cure, 320° F)			
Shore hardness A (20-min. cure)	50	54	58
Tensile (lbs. per sq. in.)			
10 min.	250	350	500
20 min.	275	330	500
30 min.	225	320	525
45 min.	225	375	500
Elongation (%)			
10 min.	320	350	530
20 min.	260	290	380
30 min.	220	250	365
45 min.	215	230	340

The tensile-elongation values of these stocks are plotted in Figure 3 as a function of the Pliolite S-1 content.
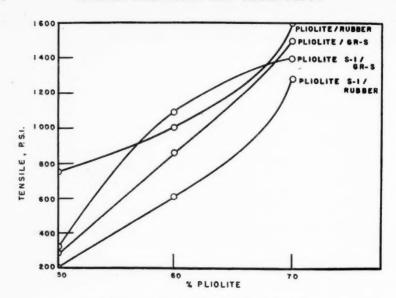
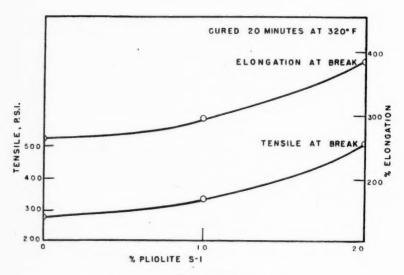FIG. 2.—Tensile properties of Pliolite-rubber mixtures.

FIG. 3.—Effect of Pliolite S-1 on GR-S gum stock properties.

In a GR-S black stock, replacement of 10 volumes Wyex black with 10 volumes Pliolite S-1 results in improved elongation, lower modulus, and equivalent tensile and hardness:

GR-S	100	100
Pliolite S-1	..	10
Wyex black	50 (27 vol.)	32.5 (17 vol. per 100 rubber)
Sulfur	1.60	1.60
Litharge	0.50	0.50
Zinc oxide	5	5
Tetramethylthiuram disulfide	0.75	0.75
Stearic acid	1	1
Paraflux	10	10
Properties (cure, 20 min. at 305° F)		
Tensile (lbs. per sq. in.)	2000	2025
Elongation (%)	440	580
300% modulus	1200	750
Shore hardness A	65	64

Pliolite S-1 and Butyl rubber are compatible when mixed on the mill.
A tough, rubberlike compound is obtained with 75 parts Butyl rubber and
25 parts Pliolite S-1. Larger quantities of resin give hard, leatherlike stocks.

MECHANISM OF CYCLIZATION REACTION

Considerable evidence is now available to indicate that the isomerization
of natural rubber and polyisoprene proceeds according to the following cycliza-
tion procedure:

Other structures for the product have been proposed by Bruson, Sebrell,
and Calvert[9]:

and by Powers[19]:

The first mechanism agrees with the type of cyclization which Tiemann[20] observed in the terpene series when he converted geraniolene into a mixture of α- and β-cyclogeraniolene, using sulfuric acid as the catalyst:

Bloomfield[21] proposed a similar mechanism for the cyclization of dihydromyrcene in the presence of sulfuric acid–acetic acid:

When natural rubber or synthetic polyisoprene is isomerized by a cyclization catalyst such as chlorostannic acid, the following changes in properties are observed: (1) increase in specific gravity; (2) increase in refractive index; (3) decrease in unsaturation, as measured by infrared absorption, iodine number, and percentage acetic acid formed by chromic acid oxidation to approximately half of the original value; (4) disappearance of the $\begin{array}{c} R \\ R_1 \end{array} C = C \begin{array}{c} H \\ R_2 \end{array}$ type of double bond, by infrared absorption data; (5) no change in C_5H_8 empirical formula, except for a small amount of combined chlorine in the resin; (6) lower molecular weight, as determined by intrinsic viscosity measurements; and (7) increase in heat distortion point.

Most of these changes can be explained by the cyclization reaction mechanism proposed. The increase in specific gravity and refractive index is usually found when simple organic molecules are cyclized. For instance, the proper-

ties of 1,5-hexadiene and the corresponding cyclized compound, cyclohexene, are compared:

	Density (d_4^{20})	Refractive index
1,5-Hexadiene	0.688	1.404
Cyclohexene	0.810	1.445

Kurtz and Lipkin[22] developed an interesting correlation of density to structure in hydrocarbon materials and showed that the increase in density in cyclorubber was close to the theoretical value.

Calculations of specific refraction show a close correlation between actual and theoretical values for both natural rubber and polyisoprene and their cyclized products:

Compound	Density (d_4^{25}) corrected	n_D^{25}	Specific refraction	
			Calculated	Found
Natural rubber	0.92	1.520	0.333	0.330
Polyisoprene	0.92	1.520	0.333	0.330
Pliolite	0.96–0.98	1.545	0.320	0.328–0.322
Pliolite S-1	0.96–0.98	1.535	0.320	0.324–0.318

The density values for the pure cyclized hydrocarbons are not accurately known because of the variable amount of high density stannic oxide present in the commercial products, but they are believed to lie in the range indicated. The calculated values for specific refraction were obtained from atomic refraction values given by Glasstone[23]. The rubbers were assumed to be linear polymers of isoprene with the unit structure $-CH_2-C(CH_3)=CH-CH_2-$. The cyclized rubbers were assumed to have the structure given in the proposed cyclization reaction. The density and refractive index values were substituted in the Lorentz-Lorenz equation to obtain the found values. The good agreement obtained is considered further proof for the cyclization reaction mechanism proposed.

Analysis by infrared absorption[24] of natural rubber and polyisoprene shows a great similarity in structure. Analysis after cyclization also shows marked similarity. The main change taking place is a great reduction in the number of double bonds. Moreover, the infrared data indicate that the structure

$$\begin{array}{cc} R_1 & H \\ \diagdown & \diagup \\ & C=C \\ \diagup & \diagdown \\ R_2 & R_3 \end{array}$$ originally present in the rubber disappears after cyclization.

This is in complete agreement with the cyclization mechanism proposed in this paper.

Natural rubber by the chromic acid oxidation method[18] produces 66 per cent acetic acid (75 per cent of theoretical value). Polyisoprene gives 59 per cent acetic acid (67 per cent of theoretical). The corresponding cyclized products gave 24–30 per cent acetic acid for Pliolite and 25–28 per cent for Pliolite S-1, or approximately 40–45 per cent of the original values. These results are in fair agreement with iodine number analyses, which show about half of the original unsaturation (Table I).

Pliolite and Pliolite S-1 solutions are much less viscous then the corresponding rubber solutions; the final viscosity values are as low as 0.05–0.001 of the

original. Intrinsic viscosity measurements in dilute benzene solutions show a considerable drop:

Rubber	Intrinsic viscosity	
	Before reaction	After reaction
Natural rubber	4.45	0.49
Polyisoprene	1.51	0.36

The decrease in chain length resulting from the cyclization reaction proposed is not sufficient to account for the drastic reduction in the viscosity obtained. It is entirely possible that there was considerable chain scission as well as cyclization in the overall reaction. Another possibility, which Staudinger[25] proposed for chlorinated rubber, is the cyclization of long side chains with the main chain, which would produce a marked shortening of the chain. This reaction is more likely for polyisoprene than for natural rubber, since the former is known to have a more highly branched chain structure than rubber.

It is interesting to compare the relative ease of isomerization of GR-S, polyisoprene, and natural rubber. Endres[8] reported that the cyclization of GR-S takes place at 160–180° C with chlorostannic acid catalyst in phenol, cresol, etc. However, polyisoprene and natural rubber cyclize very readily at 70–80° C with the same catalyst in benzene solution. The difference in reactivity can probably be attributed to the presence of methyl groups attached to unsaturated carbon atoms, which may favor closing of the ring in the cyclization reaction outlined.

CHLORINATED ISOPRENE POLYMERS

The use of natural rubber for producing chlorinated rubber was drastically curtailed during World War II. As GR-S and other synthetic rubbers became available, their use as starting materials for chlorinated products received intensive study. The preparation and properties of chlorinated GR-S were described by Endres[8]. Medvedchuk, Aldoshin, Marovich and Repman[26] found that the reactions of sodium–butadiene rubber with iodine, iodine chloride, and thiocyanogen were slower than those of natural rubber. The absence of a methyl group attached to the double bond was considered a significant factor. Our results show that synthetic polyisoprene and isoprene copolymers behave similarly to natural rubber in the chlorination process, whereas GR-S requires special handling. For purposes of direct comparison with natural rubber, the following description is limited to the chlorination of polyisoprene and the properties of the chlorinated product, Pliochlor.

CHLORINATION OF POLYISOPRENE

Polyisoprene suitable for chlorination can be made in emulsion using essentially the GR-S type of polymerization recipe with the modifier content adjusted to give a rubber of 40–45 Mooney viscosity. The latex is coagulated in the usual manner with salt–sulfuric acid and protected with an antioxidant, such as 0.5–1.0 per cent phenyl-β-naphthylamine. If desired, the rubber can be caustic-washed to free it of fat acid and other nonrubber components. Such treatment is usually given natural rubber to remove proteins, fat acids, etc. Other methods of coagulation, such as alcohol, alum, barium chloride, magnesium chloride, calcium chloride, and freezing, were also used successfully for laboratory work. Nondiscoloring antioxidants can be used, particularly if very light-colored products are desired.

When polyisoprene is dissolved for chlorination, such as in a 5 per cent carbon tetrachloride solution, an extremely viscous, gelled solution is obtained. To facilitate chlorination to a product in the useful viscosity range of less than 150 centipoises, it was found advisable to lower the initial solution viscosity. The simplest but most time-consuming method is to allow the solution to age in the presence of oxygen and light until the desired viscosity has been reached (Figure 4). In this respect polyisoprene closely resembles natural rubber,
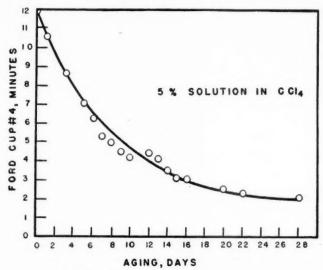
FIG. 4.—Effect of aging on viscosity of polyisoprene solution.

whereas GR-S shows relatively little change. This degradation takes place either in the presence or absence of the conventional antioxidant.

This decrease in viscosity can be greatly increased by heat and the addition of a peroxide. For instance, a polyisoprene solution, which initially was too viscous to measure, had dropped to a Ford cup No. 4 viscosity of 1.7 minutes after heating for 30 minutes at 68° C with 1 per cent benzoyl peroxide.

The most practical way to break down polyisoprene to give low viscosity solution is to hot mill (Figure 5) the rubber, reducing the Mooney value to 20 or below. An alternative procedure is to masticate the rubber at 250–300° F in a Banbury mixer. Cold processing has relatively little effect on cement viscosity. The following table gives the solution viscosity in a 5 per cent carbon tetrachloride solution of polyisoprene given these treatments:

Treatment	Viscosity, Ford Cup No. 4 (min.)
Banbury (15 min. at 215° F)	0.78
Hot milling (90 min.)	0.65
Cold milling (210 min.)	16.5

Carbon tetrachloride, the ideal chlorination solvent, was found entirely suitable for polyisoprene, as it was for natural rubber. Other solvents were tried, such as benzene, chlorobenzene, chloroform, and ethylene dichloride, but all have the disadvantage of reaction with chlorine; in most cases they give byproducts which are difficult to remove from the product.
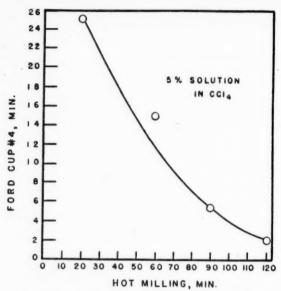
FIG. 5.—Effect of milling on polyisoprene solution viscosity.

A 5 per cent by weight concentration in carbon tetrachloride was adopted as a standard procedure for laboratory chlorination. Concentrations as high as 8–9 per cent were run, but they require powerful agitation, particularly during an intermediate gel stage usually obtained with polyisoprene and natural rubber.

A temperature of 25–50° C was employed for most of the laboratory chlorinations. Some carried out at 10–15° during the first part of the chlorination also behaved satisfactorily. Higher temperatures can be utilized, but have the disadvantage of lower chlorine solubility in the solvent unless the pressure is increased. Since the reaction is exothermic and a large volume of hydrogen chloride is given off in the first part of the reaction, a chlorination temperature of 25–40° C is most convenient, and can be readily regulated by the use of cold tap water. No significant change in the properties of the product can be attributed to a temperature variation in the range mentioned.

The presence of oxygen has a pronounced effect on the chlorination reaction. Apparently its action is twofold: depolymerization, which reduces the molecular weight and viscosity, and chlorination catalyst, which is of particular value in obtaining highly chlorinated products. Both of these factors are illustrated in the following chlorination carried out in darkness and in the absence of oxygen. The batch was split and half aged in darkness. The other half was aged in darkness 16 hours while a slow stream of oxygen was bubbled in:

Conditions	Initial viscosity (min.)	Product viscosity (centipoises)	Chlorine (percentage)
Dark	1.62	280	58.11
Dark and oxygen	1.62	25	59.82

The addition of controlled amounts of oxygen during chlorination is unquestionably the most practical way of controlling product viscosity as well

as shortening chlorination time. However, alternative methods of operation are available if desired. For example, the rubber can be thoroughly broken down before solution to give a low initial viscosity, as in the following, which was Banbury-treated for 34 minutes at 215° F. Chlorination was carried out in the dark and without oxygen for 4 hours, followed by an aging period of 22.5 hours. From a solution with an initial Ford cup viscosity of 0.32 minute a product was obtained of 53 centipoises viscosity and 59.39 per cent chlorine. Another possibility is to break down a viscous solution by peroxide treatment before chlorination. In one case a viscous polyisoprene solution was heated at 70° C for 11 hours with 1 per cent benzoyl peroxide and then chlorinated as described. From a solution with initial viscosity of 0.375 minute a product was obtained after 21.5 hours' aging with 102 centipoises viscosity and 59.1 per cent chlorine. A third possibility is to prepare a very low Mooney rubber which requires no milling breakdown. Polyisoprene with a Mooney value of 7 gave a solution with Ford cup No. 4 viscosity of 0.41 minute which was chlorinated and worked up immediately. The product had a viscosity of 123 centipoises and 57.64 per cent chlorine. This method is impractical because our synthetic rubber plants cannot handle a polymer in this Mooney range.

In conclusion, a chlorinated polyisoprene in the desired viscosity range can be obtained without admission of oxygen during chlorination, if the initial solution viscosity is below about 0.50-minute Ford cup No. 4 viscosity for a 5 per cent carbon tetrachloride solution. However, it is questionable whether products containing more than 60 per cent chlorine can be consistently obtained without oxygen, unless a fairly long aging period of at least 16 hours is resorted to.

The effect of visible light on the chlorination reaction is a minor one, for it is certain that the reaction can be carried out satisfactorily in total darkness, particularly if oxygen is present. Comparable laboratory reactions gave the following results:

Conditions	Initial viscosity (min.)	Aging (hrs.)	Product viscosity (centipoises)	Chlorine (percentage)
Light, no oxygen	1.36	24	124	58.1
Dark, no oxygen	1.62	24	280	58.1

Although light was a beneficial factor in our laboratory chlorinations, it cannot be demonstrated that light does anything to the reaction which traces of oxygen will not do more rapidly and efficiently.

The effect of aging on the viscosity (Figure 6) and chlorine content of the product is difficult to evaluate because oxygen and light also influence these properties to a marked degree. There is no question that reaction during aging in darkness and in the absence of oxygen is slow; it does, nevertheless, continue. But it is questionable whether very much depolymerization can be carried out during the final stages of the reaction unless some oxygen is present.

The effect of metal contamination was studied. It was established that nickel has no effect on the chlorination process or the stability of the product. Chlorination in the presence of iron filings proceeded in the normal fashion but, when the solution was degassed by heating, it gelled and turned black, with evolution of hydrogen chloride. If water or soda ash was added before heating, this condition was avoided but a darker-colored product was obtained. Evidently if the ferric chloride formed during chlorination is not destroyed before heating, it acts as a cyclization catalyst and causes cross-linking, with subsequent gelation of the solution.

After the reaction has proceeded to the desired viscosity and chlorine content, degassing by heating the solution with agitation at the reflux point stops further reaction. Addition of 1–2 per cent soda ash, with subsequent heating, removes the last traces of free acid and, possibly, some loosely held chlorine in the product. The solution may be filtered, preferably with the addition of a filter aid, and is then ready for isolation of the product.

A number of methods are available for isolating Pliochlor as the pure solid. The carbon tetrachloride solution may be slowly added, with agitation, to a nonsolvent such as alcohol or gasoline, with subsequent filtration, washing,

POLYISOPRENE·
CHLORINATED IN
5% CCl_4 SOLUTION
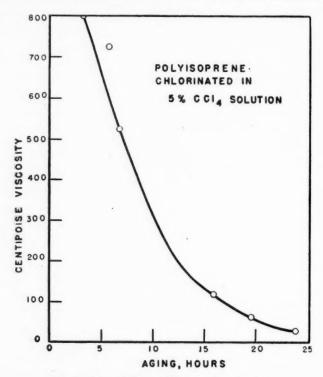
Fig. 6.—Effect of solution aging on product viscosity.

and drying. A second method is to vacuum-distill the chlorinated solution until all the carbon tetrachloride has been removed. The third and possibly best method is to remove the solvent by steam distillation. This method removes the solvent completely with no loss of product, and has the further advantage of producing a more stable product. The steam-quenched product, after separation from the water phase, can be readily washed, dewatered by centrifuging, and finally dried at 70–75° C in a circulating air oven.

CHLORINATION OF RUBBER AND POLYISOPRENE

For as direct a comparison as possible, polyisoprene and natural rubber of the same plasticity were chlorinated under identical conditions, and samples were removed at various intervals for analysis. Pale crepe, which had been

factory-milled to a Williams plasticity of 68, was given a further laboratory cold milling of 5 minutes. Polyisoprene of 40 Mooney was hot-milled for 80 minutes. A comparison follows of the acetone extract, intrinsic viscosity, and Ford cup viscosity of a 5 per cent carbon tetrachloride solution of the polymers to be chlorinated:

Polymer	Acetone extract (%)	Intrinsic viscosity	Solution viscosity Ford cup (min.)
Rubber	2.1	1.23	0.83
Polyisoprene	3.8	1.13	1.08

Solutions containing 125 grams of rubber and 1,500 cc. of carbon tetrachloride were prepared, and chlorine was bubbled in at the rate of 1.2 grams per minute at 35° C, with agitation. Five samples from each were removed at the time intervals noted in Table III. After a sample was siphoned out, it was allowed

TABLE III

COMPARATIVE CHLORINATIONS OF POLYISOPRENE AND RUBBER

Chlorination time (hrs.)	Gross chlorine input (g.)	Chlorine (%)	Product viscosity (centipoises)	Stability (min.)	Color	Iodine no.	Soft point (° C)	Intrinsic viscosity
				Polyisoprene				
0	..	..	..	..	..	364		1.13
1.85	133	37.2	Insol.	0	Brown	118.9	30.0	(73% gel)
3.05	220	53.2	Insol.	2	Tan	35.2	58.5	(29% gel)
4.48	323	63.4	146	2	Cream	2.4	87.0	0.39
5.22	376	64.1	137	2	Cream	1.9	92.5	0.36
6.22	448	65.8	105	4	Cream	0.6	94.0	0.31
				Natural rubber				
0	..	..	..	..	..	357	..	1.23
1.85	133	38.3	Insol.	1.5	Red-brown	135.8	35.5	(87% gel)
3.17	228	57.9	Insol.	4	Light brown	14.2	44.0	(21% gel)
4.27	307	70.4	670	4	White	1.25	104.5	0.49
5.00	360	69.5	300	4	White	1.20	97.5	0.41
6.00	432	70.8	77	2.5	White	1.25	99.0	0.19

to age at room temperature for 30 minutes and then was degassed by refluxing; the product was isolated immediately by steam distillation. The final sample was allowed to age overnight (16–18 hours) before being worked up. The chlorinations proceeded in a similar manner. In each case there was some increase in viscosity until a gel stage was reached. Finally the gel (which appeared after the first two samples were removed) went into solution and a smooth, fairly thin solution resulted. The first portion of the reaction was exothermic in nature and liberated a large amount of hydrogen chloride—in fact, there is good evidence that only substitution takes place in the first part of the reaction. No oxygen was intentionally added, but probably traces were present to aid the reaction.

Table III summarizes these parallel chlorinations and compares various properties of the products. It is evident that a great similarity exists in the two systems. As the chlorine content increases, the product goes through an insoluble stage and then forms soluble products of decreasing centipoise viscosity value. With increasing chlorination the color of the product becomes lighter, the iodine number rapidly decreases and finally drops to practically zero, the softening point increases, and the molecular weight (as measured by

intrinsic viscosity) decreases regularly once the gel stage has been passed. The lower final chlorine value for polyisoprene is probably related to differences in the structures of the two polymers.

The data in Table III are plotted as a function of chlorination time in Figure 7 (chlorine content), Figure 8 (product viscosity), Figure 9 intrinsic viscosity), Figure 10 (iodine number), and Figure 11 (softening point).
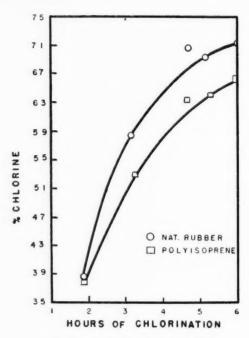

FIG. 7.—Comparison of rates of chlorination.

PROPERTIES AND USES OF PLIOCHLOR

The properties of Pliochlor are similar to those of chlorinated natural rubber. By proper control of the various factors mentioned, products of 60–70 per cent chlorine content and centipoise viscosity of 10 to 150 or more can be consistently obtained. The product viscosity, as measured for a 20 per cent toluene solution on the Ford cup No. 4 at 25° C, is obtained from the following values:

Ford-cup No. 4 (min.)	Product viscosity (centipoises)
0.22	10
0.26	20
0.30	30
0.33	40
0.37	50
0.45	70
0.56	100
0.61	115
0.67	130
0.74	150

Fig. 8.—Effect of chlorination on product viscosity.
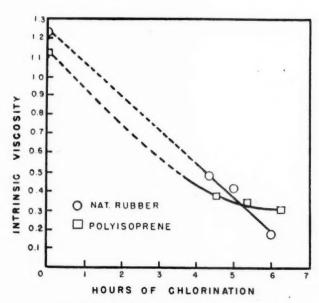
Fig. 9.—Effect of chlorination on intrinsic viscosity.
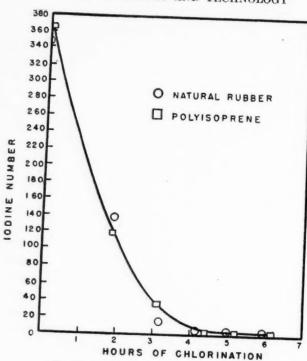
FIG. 10.—Effect of chlorination on iodine number.
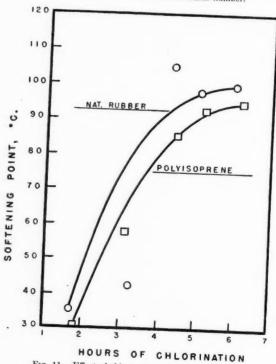
FIG. 11.—Effect of chlorination on softening point.

The color of the product is white to cream, depending on the kind and amount of antioxidant originally present, and its solutions are correspondingly very light amber to brown in color. It is readily soluble in benzene, toluene, xylene, chloroform, carbon tetrachloride, ethylene dichloride, ethyl acetate, and methyl-ethyl ketone. Acetone partly dissolves it, and dibutyl ether swells it without dissolving. Methyl alcohol, ethyl alcohol, butyl alcohol, gasoline, kerosene, and acetic acid are nonsolvents.

The thermal stability of Pliochlor and chlorinated rubber prepared under the same conditions is comparable. Three grams of product are completely dissolved in 7 grams of xylene in a 1×6 inch test tube at room temperature. The tube is placed in a glycerol bath maintained at 120° C, the solution level equalized with the glycerol level. A piece of Congo red paper, $\frac{1}{4}$-inch wide, is suspended two inches above the surface of the solution. The time required for the paper to turn blue to a point one-half inch above the lower is noted in minutes and recorded as the stability value. Both products give values in the same range (2–10 minutes).

The above test is a qualitative test which merely indicates when the first amount of hydrogen chloride is liberated. A more quantitative comparison is obtained by the following method: Ten grams of chlorinated product are dissolved in 19.5 ml. of α-chloronaphthalene in a 1×8 inch test tube, which is then heated in a glycerol bath for 1 hour at 175° C. A standard amount of dry air (6 liters) is bubbled through the solution and into a standard caustic solution, which is then titrated with standard acid. The stability is calculated as the per cent hydrogen chloride released in 1 hour. By this method a sample of chlorinated rubber gave 0.369 and Pliochlor gave 0.420 per cent.

The stability of Pliochlor can be greatly increased by the incorporation of small amounts of insoluble neutralizing agents, such as calcium carbonate or magnesium oxide, and preferably by the addition of soluble ethylene oxide derivatives which readily add hydrogen chloride to form the chlorohydrin[27]:

Stabilizer	Percentage added	Stability (min.)
Control	..	10
Magnesium oxide	3	427
Styrene oxide	1	23
Styrene oxide	3	48
Styrene oxide	5	71
Epichlorohydrin	1	76
Epichlorohydrin	3	365
Epichlorohydrin	5	Over 511

Pliochlor can be milled for a short time without decomposition, but it is usually advisable to add a stabilizer, such as 5 per cent styrene oxide. The milled material, in the form of a clear amber sheet, can be ground and molded for 10 minutes at 260° F to produce a light-colored, translucent test-piece.

The softening point of Pliochlor ranges from 94° to 124° C, depending on the chlorine content and type of polyisoprene used.

The ash content of Pliochlor varies from 0.1 to 0.8 per cent, depending on the method of coagulation used in preparing the rubber.

The apparent specific gravity of unmilled powder is only 1.21 to 1.26 because of occluded air. A true value of 1.45 to 1.55 on the milled, ground resin is obtained, depending upon the chlorine content.

Pliochlor is apparently saturated, as judged by a negligible iodine number (approximately 1 or less) and infrared absorption data[24]. However, a small amount of residual unsaturation could be present, since the iodine number

analysis is probably affected by the large amount of chlorine present, and the infrared method is not sensitive enough to detect a small amount of unsaturation.

Fractional precipitation of Pliochlor dissolved in methylethyl ketone by the addition of methyl alcohol in regulated amounts, and determination of intrinsic viscosity in dilute benzene solution of the individual fractions, indicated a wide range of molecular weights in the original sample:

Sample	Intrinsic viscosity
Original	0.39
Cut I (31%)	0.52
Cut II (41%)	0.28
Cut III (16%)	0.11

Pliochlor shows the same wide range of compatibility with plasticizers and resins as does chlorinated rubber. For instance, it is compatible with dibutyl phthalate, dioctyl phthalate, tricresyl phosphate, diamylnaphthalene, dibutyl tartrate, glyceryl triacetate, Santicizers M-17 and B-16, perilla oil, linseed oil, Kapsol, Kronisol, Hercolyn, Cumar MH-1 and P-25, Methox, Rezyl 784-1, Bakelite 4503 and XJ-9868, Chlorowax 70, Aroclor 1248, 1260, 1268, and 5460, and Glyptals 2500 and ZV-3507, ZV-3293, ZV-3320, and ZV-3488. It is incompatible with oleic acid, chinawood oil, bodied dehydrated castor oil, blown soybean oil, Vistac, Vistanex, Butyl rubber, and Glyptals ZV-3451, ZV-3471, and ZV-3264.

Tests with corrosive agents show that Pliochlor compares favorably with chlorinated rubber in resistance to concentrated hydrochloric acid, concentrated sulfuric acid, concentrated and fuming nitric acid, and chromic acid solution. Both are darkened by fuming sulfuric acid.

Pliochlor, in general, can be used for the same purposes as chlorinated rubber, such as protective coatings, printing inks, and rubber-to-metal adhesives. Satisfactory rubber-to-metal adhesions were obtained with various rubber stocks to soft steel, brass, cast iron, aluminum, stainless steel, and bronze. For these measurements a test method[28] adapted from A.S.T.M. Designation D429-39 was employed. The following table gives a summary of results with an adhesive cement in which chlorinated polyisoprene and chlorinated rubber were compared directly on four different rubber stocks:

		Adhesion data (lbs. per sq. in.)		
Adhesive	Neoprene	Nitrile rubber	GR-S	Natural rubber
Chlorinated polyisoprene	1175*	837*	432	313
Chlorinated rubber	440	913	410	430

* Substantial failure in the stock.

The synthetic product gave best results with the synthetic stocks, and the natural rubber product was better on a natural rubber stock.

MECHANISM OF CHLORINATION REACTION

Since rubber and synthetic polyisoprene have substantially the same chemical structure as far as the repeating unit in the chain is concerned, it is reasonable to assume that they both chlorinate by the same mechanism. Kirchhof[29] suggested that in rubber chlorine first adds to the double bond. One or two molecules of hydrogen chloride are then split off, and chlorination results in a mixture of $(C_5H_6Cl_4)_x$ and $(C_5H_7Cl_3)_x$, which contain 68 and 61.5 per cent

of chlorine, respectively. Commercially chlorinated rubber contains 66–68 per cent of chlorine and may be considered to be a mixture of these two products with an empirical formula of approximately $(C_{10}H_{13}Cl_7)_x$, which McGavack[30] previously proposed for highly chlorinated natural rubber.

Two recent papers by Bloomfield[31] have thrown considerable light on this mechanism. The probable course of reaction with natural rubber involves a completely substitutive initial reaction, followed by simultaneous substitution and addition, and terminated by substitution:

$$C_{10}H_{16} + 2Cl_2 \rightarrow C_{10}H_{14}Cl_2 + 2HCl \ (34.6\% \ Cl)$$
$$C_{10}H_{14}Cl_2 + 2Cl_2 \rightarrow C_{10}H_{13}Cl_5 + HCl \ (57.2\% \ Cl)$$
$$C_{10}H_{13}Cl_5 + 2Cl_2 \rightarrow C_{10}H_{11}Cl_7 + 2HCl \ (65.4\% \ Cl)$$

Confirmation of this mechanism is given by carbon-hydrogen analyses of Schidrowitz and Redfarn[32]; the analyses agree with a carbon-hydrogen analysis of $C_{10}H_{11}$ rather than $C_{10}H_{13}$. The lower than theoretical unsaturation, as measured by iodine value during the first part of the reaction, is attributed partially to steric hindrance of chlorine in the product and also to a simultaneous cyclization reaction:

Comparison of this mechanism with the one given for the cyclization of dihydromyrcene shows a striking similarity.

Bloomfield, in a more recent paper[33], finds no evidence for substitutive chlorination at the ethylenic carbon atom. If the reaction proceeds in a strictly substitutive manner, it is more likely that reaction takes place at the α-methylene group in the system $-CH_2-C(CH_3)=CH-$. He finally concludes, however, that the most probable mechanism involves the initial formation of an activated additive dihalide, which then simultaneously loses hydrogen chloride and forms a cyclic monohalide.

Staudinger[25] visualizes chlorinated rubber as a highly chlorinated cyclorubber or, more specifically, as a highly chlorinated, branched polycyclic polyterpene. He suggests two types of ring structure: a six-membered ring

formed through the side methyl groups by loss of hydrogen chloride, and cyclization of long side-chains with the main chain, which markedly shortens the chain length. He concludes from osmotic molecular-weight determinations that chlorinated rubber is of the same order of molecular magnitude as the original rubber. He attributes the molecular weights of relatively low viscosity to the presence of short, compact molecules formed by cyclization reactions.

Staudinger's theory that chlorination involves cyclization of long side-chains with the main chain is probably even more applicable to synthetic polyisoprene than to rubber, since there is fairly definite proof that emulsion polymers as ordinarily prepared contain a considerable proportion of branched polymers, whereas structural studies of natural rubber failed to give positive proof of the presence of long side-chains. However, the enormous effect of traces of oxygen during the chlorination of both rubber and polyisoprene in solubilizing the gel stage and reducing product viscosity seems ample evidence to the authors that oxidative degradation plays an important role in the reaction.

A comparison of the infrared absorption spectra of Pliochlor and chlorinated rubber shows a great similarity[24]. No double bonds are present and the C-H spectra is drastically reduced. The characteristic absorption for the methyl group practically disappears; this means either that it is absent in the product or, more likely, that it is still present but its absorption characteristics have been overshadowed by the large number of neighboring chlorine atoms.

HYDROCHLORINATION OF ISOPRENE POLYMERS

Rubber hydrochloride has been marketed for a number of years as Pliofilm, and has found widespread use as a film material, particularly in the food-packaging field[34]. Weber[35] reacted rubber and hydrogen chloride in 1900 and obtained the product, $(C_{10}H_{18}Cl_2)_x$. Harries and Fonrobert[36] described the successful hydrohalogenation of natural rubber, gutta-percha, synthetic polyisoprene, and polydimethylbutadiene. Whitmore[37] reports that isopropylethylene shows no reaction with hydrochloric acid in months, whereas trimethylethylene and 2-methyl-1-butene, both of which have a methyl group attached to an unsaturated carbon atom, react rapidly with the same reagent.

Our experience has been that polybutadiene, butadiene-styrene, and butadiene-acrylonitrile copolymers do not add hydrogen chloride. Polyisoprene and isoprene copolymers, however, greatly resemble natural rubber in the rapid addition of hydrogen chloride.

Rubber and isoprene polymers readily add hydrogen chloride in benzene or chloroform solution. In carbon tetrachloride the reaction is much slower and is incomplete:

Polymer	Solvent	Chlorine in product (%)
Polyisoprene	Benzene	26.87
Isoprene/styrene 50/50	Benzene	16.91
75/25	Chloroform	23.15
75/25	Carbon tetrachloride	5.10

The theoretical chlorine content of polyisoprene hydrochloride $(C_{10}H_{18}Cl_2)_x$ is 33.97 per cent. When completely reacted, synthetic polyisoprene hydrochloride reached a chlorine content of 28.14 per cent (corrected for 4.5 per cent of nonrubber components), which is 83 per cent of the theoretical value. The difference of 17 per cent is probably due largely to the presence of nonreactive

side vinyl groups formed by 1,2-addition polymerization of isoprene. Side isopropylidene groups formed by 3,4-addition probably add hydrogen chloride because of the methyl group attached at the double bond:

1,2-addition   3,4-addition

Natural rubber hydrochloride can be obtained with a maximum of 95 per cent of the theoretical chlorine content. On the basis of this low chlorine value and lower than expected molecular weight from viscosity measurements, Staudinger[25] considers the product to consist of chlorinated paraffinic chains with branchings and undetermined terpenelike rings in several positions.

In the preparation of rubber hydrochloride, the product passes through a ripening period after saturation with hydrogen chloride, in which it is converted from an amorphous, rubberlike material to a solid, crystallized product suitable for films. If the reaction is carried too far, it becomes insoluble, a condition caused by condensation or cross-linking reactions not considered by Staudinger. On the other hand, synthetic polyisoprene does not show this ripening phenomenon, and remains as a soluble rubberlike product, with poor film characteristics. The product, however, has a low moisture vapor transmission rate, comparable to amorphous rubber hydrochloride, and, when it is suitably compounded, it can be used in moistureproof coatings.

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OBSERVATIONS ON THE ACTION OF UNSATURATED COMPOUNDS ON RUBBER IN SOLUTION *

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At the time Le Bras and one of the present authors[1] pointed out the possibility of combining unsaturated compounds with rubber in the form of latex or by an ordinary mixing operation, reference was made to an interesting work, published by Bacon and Farmer[2] in 1938, in which these authors described the addition of maleic anhydride to rubber in solution. At the same time it was emphasized, and this point was taken up in more detail in a later publication of Le Bras[3], that there are essential differences between the products obtained by the two methods, both with respect to their appearance and their properties, according to whether the technique employed is emulsion or mixing, or is that described by Bacon and Farmer. It should be borne in mind that the most distinguishing feature is that the first type of product is always to a great extent insoluble in solvents of rubber, whereas the second type of product may still be soluble even when 10–15 per cent, for example, of maleic anhydride has become fixed by the rubber.

However, in spite of the products differing in certain attributes, the reactions involved in these two different experimental techniques should be fairly similar. Accordingly, in attempting to increase the action of these reagents on rubber, both in the form of latex and in solid admixture, and to throw further light on the mechanism of the reaction, the present authors have studied the effect of the reagents under the operating conditions employed by Bacon and Farmer, i.e., in solution. In what follows, various observations are reported which may contribute to a better understanding of certain peculiarities of this last type of reaction and to its wider application.

GENERALIZATION OF THE REACTION BETWEEN MALEIC ANHYDRIDE AND RUBBER IN SOLUTION

Bacon and Farmer have described in detail the addition of maleic anhydride to rubber in the presence of a catalyst, viz., benzoyl peroxide. Although their experiments were confined to this one reagent, by taking cognizance of the fact that maleic anhydride must react through its double bond, which is known to be highly reactive, they were led to the conclusion that other organic compounds of similar structure should be capable of reacting in the same way.

As a matter of fact, a recent patent[4] claims the use of reaction products of rubber with polybasic organic acids possessing an active double bond or reaction products with the corresponding acid anhydride. One of the examples in this patent refers particularly to the addition product of aconitic acid (carboxy-3-pentene-2-dioic acid) with rubber. Combination is carried out in

solution, as in the technique of Bacon and Farmer. This represents the first case of an extension of the reaction described by these authors. For other reasons the present authors have had occasion to study, under the experimental conditions used by Bacon and Farmer, the behavior of citraconic anhydride (I) and itaconic anhydride (II):

$$
\begin{array}{cc}
HC = CCH_3 & H_2C - C = CH_2 \\
OC \quad CO \quad (I) & OC \quad CO \quad (II) \\
O & O
\end{array}
$$

No positive results were obtained with citraconic anhydride, but it is possible that the optimum conditions were not realized. Itaconic anhydride combined with rubber, but the yield was only half that obtained with maleic anhydride under the same conditions.

The reaction which deserved particular attention, however, was that of vinyl monomers, which were found to be capable of reacting with rubber both in emulsion form and on a mill. The reaction of acrylonitrile is particularly interesting.

The addition of acrylonitrile to rubber in solution gave yields very close to those obtained with maleic anhydride by Bacon and Farmer. For example, a mixture of a 3 per cent solution of rubber in benzene, acrylonitrile (18.5 per cent by weight of the rubber) and benzoyl peroxide (8 per cent by weight of the rubber) yielded, when heated for 18 hours on an oil bath at 100° C, a substance containing 9–10 per cent of combined acrylonitrile. Likewise a mixture of a 3 per cent solution of rubber in benzene, acrylonitrile (145 per cent by weight of the rubber), and benzoyl peroxide (1 per cent by weight of the rubber) yielded a product containing 10–14 per cent of combined acrylonitrile.

Under the same experimental conditions Bacon and Farmer obtained, with maleic anhydride, 12 and 13 per cent, respectively, of combined anhydride[5].

It is noteworthy that, under these conditions, acrylonitrile apparently combines with rubber without at the same time forming any of its own polymer (at least in the mixtures which were studied) whereas, in the absence of rubber, acrylonitrile polymerizes to a considerable degree itself, depending on the solvent. This formation of a polymer is evident by the appearance in the solution of a flocculent precipitate which is not evident when rubber is present. On the other hand the addition products of rubber and acrylonitrile which are obtained are soluble in boiling p-dichlorobenzene, whereas polymerized acrylonitrile is wholly insoluble in this solvent.

The addition products containing 10–15 per cent of acrylonitrile are still very rubbery, and can be milled and vulcanized. As was to be expected, the vulcanizates showed an increased resistance to solvents; for example, it was found that the products containing 14 per cent of acrylonitrile swelled 90–100 per cent in gasoline, whereas a control sample of vulcanized rubber which had not been modified by acrylonitrile swelled 170 per cent in the same gasoline under the same conditions.

No attempts were made to prepare addition products containing high percentages of acrylonitrile, but it should be possible to prepare them as in the case of maleic anhydride.

In the same way methacrylonitrile adds to rubber, giving somewhat smaller yields than those obtained with acrylonitrile.

These few results confirm the views of Bacon and Farmer. Because of the

great variety of vinyl monomers which are available, and because of the nature of the reaction, it is possible to foresee the successful preparation of a wide range of resins having rubber as their base. On the other hand the reaction offers a means of obtaining a wide variety of derivatives of rubber, since it offers the possibility of fixing all sorts of chemical groups on rubber.

It should be added that, just as the reaction of Bacon and Farmer can be extended to other unsaturated compounds in addition to maleic anhydride, it is likewise possible to employ other catalysts instead of benzoyl peroxide. Thus, in a British patent application[6] the reaction is simply carried out in the presence of air or oxygen; on the other hand, in one of the examples cited in the Dutch patent which has already been mentioned[4], cobalt naphthenate is used as the catalyst. Finally the present authors have succeeded in bringing about the fixation of maleic anhydride on rubber in solution, without the direct addition of a catalyst, by preliminary exposure to the simultaneous action of ultra-violet radiation and of ozone[7].

GELATION OF SOLUTIONS DURING THE REACTION AND THE SOLUBILITY OF THE PRODUCTS

The fact that the addition products are either soluble or insoluble is an important feature, for it may often be the determinant factor in the possible application of these products. Actually numerous factors have an influence on the solubility, so it is not easy, from this point of view, to understand the reaction fully.

Bacon and Farmer have shown that, in general, the solubility of rubber in solvents decreases with increase in the proportion of maleic anhydride. With high proportions, the products are insoluble; on the contrary they are soluble to some extent in solvents such as ethanol.

The present authors succeeded in obtaining addition products containing 10–15 per cent of maleic anhydride which were soluble in benzene, as is also the case with products made from acrylonitrile as well.

Bacon and Farmer have shown also that the derivatives can be redissolved more easily when they are freshly precipitated than after they have become dry. The present authors have found that, even after complete drying, their solubility changes with time; in fact, it was observed, for example, that certain products which can be easily redissolved in benzene when they have just been freed of every trace of solvent, become partially insoluble after having been stored for some time. This phenomenon is, moreover, rather indefinite; hence, it is necessary, from the practical point of view, to be certain that the product is put back into solution as rapidly as possible if it is to be used later in this form.

When the products of the reaction are heated, either after being dried or even during elimination of the solvent, e.g., heating the dried product for one hour at 100° C, they become insoluble. This seems to be a case of true vulcanization. The phenomenon was found to be true of the products tested (those from maleic anhydride and acrylonitrile), even when only a few per cent of the reagent is combined. However, the phenomenon was likewise observed with the control samples containing benzoyl peroxide but no maleic anhydride or analogous reagent, so perhaps the effect is only a more or less indirect action of the benzoyl peroxide, which, as is known, is a vulcanizing agent for rubber.

The principles which have just been outlined are inadequate to make it possible to prepare products of predetermined solubility. It has, in fact, been

found that, with the same proportion of combined maleic anhydride or acrylonitrile, successive preparations of freshly prepared .products show the most widely differing solubilities.

By considering only cases where the percentages of combined reagent are not too high, two types of products can be distinguished: (1) those which are, when freshly prepared, completely soluble in benzene, and (2) those which, when freshly prepared, swell in benzene but do not appear to dissolve in it. This distinction is related, in a general way, directly to a phenomenon which may or may not be evident during the time the reaction takes place, *viz.*, gelation.

If it were possible to recognize and to control the different factors which govern this phenomenon, it would then be possible to obtain either of the two types of derivatives.

Bacon and Farmer mention this gelation and relate it to the concentration of rubber in the solution, to the percentage of benzoyl peroxide, and to the nature of the solvent. They call particular attention to the fact that the tendency toward gelation is manifest when the concentration of rubber exceeds 3 per cent.

The present authors have studied this phenomenon by using 3 per cent solutions of rubber in various solvents, with 8 parts of benzoyl peroxide per 100 parts of rubber, and with various proportions of maleic anhydride[8]. In this way it was proved that gelation is primarily the result of a specific action of benzoyl peroxide, which reacts with rubber in solution under certain conditions.

This mode of action of benzoyl peroxide is, moreover, implicitly indicated in work by Spence and Ferry[9], who showed that various reagents, of which benzoyl peroxide is one, can either polymerize or depolymerize rubber. The present authors have, in fact, proved that in the absence of maleic anhydride or other similar reagents benzoyl peroxide can, when it acts on rubber solutions, either bring about polymerization or, on the contrary, cause degradation of the rubber. Bacon and Farmer, and before them Shimada[10], observed only a degrading effect.

The present authors have studied the factors which are capable of affecting the reaction in one sense or another. Advantage was taken of the work of Spence and Ferry and of the more recent work of Stevens[11] and of Naunton[12] dealing with the formation of photogels. The results of the work lead to the following conclusions.

The solvent has a very pronounced influence, as is also known to be the case of photogelation. With respect to the ease with which gelation takes place the following representative types of solvents decrease in the following order of effectiveness: carbon tetrachloride > benzene > toluene > *p*-dichlorobenzene.

In the cold and with exposure to light, benzoyl peroxide causes degradation of the rubber, whereas, when acting alone, light brings about gelation of the solutions[13].

When hot, *e.g.*, at the boiling point of the solvent, and in darkness, benzoyl peroxide brings about gelation of solutions rapidly; with exposure to light, the reaction proceeds according to the intensity of the light, *i.e.*, toward polymerization or toward depolymerization. It was observed also, in an experiment in which the intensity of the illumination was varied greatly, that gelation was followed by peptization of the gel, and that, when the product was ex-

tracted from the solution, it was obtained in final form as a highly depoly-merized rubber which was almost liquid.

When air was bubbled through the solution during the reaction, an advanced stage of degradation was reached in every case.

The less rubber was masticated before solution, the greater was the tendency toward subsequent gelation.

It was not possible to be sure, *a priori*, whether these phenomena always proceed in the same way in the presence of maleic anhydride or other compounds containing active double bonds. It seemed advisable to verify this point, and it was found to be true of maleic anhydride and, to a certain extent, of acrylonitrile as well.

For example, when a mixture of a 3 per cent solution of rubber in benzene, maleic anhydride (18.5 per cent by weight of the rubber), and benzoyl peroxide (8 per cent by weight of the rubber) was heated, the following results were obtained.

(1) In darkness total gelation took place, with formation of an insoluble product.

(2) With exposure to light (average illumination), gelation did not take place, but the product, although at first soluble, became insoluble after complete drying.

(3) With exposure to light and simultaneous bubbling of air through the reaction mixture, gelation did not take place, and the product remained soluble after having been completely dried.

In this last case, the control sample prepared in the absence of maleic anhydride was a highly degraded rubber which was almost liquid. The addition product itself was relatively hard, and when masticated, formed a smooth transparent film, which was very pliable but which withstood only slight stretching.

When the reaction was carried out in toluene instead of in benzene, and with exposure to light but without bubbling air into the reaction solution, the product remained soluble after having been dried.

As a result of these various observations, it may therefore be concluded that, for any particular reaction mixture, the reproducibility of the reaction can be assured only if the factors which bring about oxidation, *i.e.*, light and contact with air, are maintained constant.

As a final conclusion, a comparison of the addition products obtained by carrying out the reaction in solution, under conditions such that gelation caused by benzoyl peroxide cannot take place, with those conditions incurred in simple cold mastication of a mixture of rubber and maleic anhydride[14], differences of a particularly marked character are evident, which are probably attributable to differences in structure.

In the first case, the products are soluble, and physically resemble in certain ways other substances such as chlorinated rubber and rubber hydrochloride. In the second case, the products are true vulcanizates, which are insoluble even when they contain the smallest percentages of combined maleic anhydride.

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THE VARIATION OF COMPOSITION OF 40 : 60 ISOPRENE-STYRENE COPOLYMERS WITH CONVERSION *

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There is little published work dealing with the emulsion copolymerization of isoprene and styrene[1]. In ascertaining the effect of varying conditions on the emulsion copolymerization of a 40:60 mixture of isoprene and styrene, an approximately equimolecular mixture, it was observed that the initially formed copolymer contained about 80 per cent of styrene. As the reaction was continued to maximum conversion, the styrene content decreased to approximately 60 per cent. These results show that at this monomer ratio styrene enters the copolymer faster than does isoprene. This behavior is similar to that of styrene when copolymerized with acrylonitrile and with vinylidene chloride[2]. The evidence indicates also that the copolymer is not homogeneous with respect to composition.

Procedure.—The most satisfactory polymerization recipe in parts by weight was: isoprene, 40; styrene, 60; water, 200; potassium persulfate, 0.30; sodium oleate, 20; dodecanethiol, 0.25. The experiments were carried out with 10 grams of monomers in 50-cc. test-tubes[3] which had been cleaned with concentrated nitric acid and which were seated on a rotating shaft and turned end over end in an insulated water-bath at 40°.
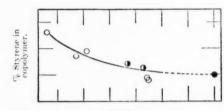
After agitation for the specified time, the latex was steam distilled to remove unchanged monomers, and the polymer was coagulated with 0.6 M hydrochloric acid. The tough, rubbery coagulum was cut into small pieces to facilitate removal of acid, then dissolved in benzene containing phenyl-β-naphthylamine in an amount equal to 2 per cent by weight of the polymer. The benzene solution was dried by calcium chloride, and the polymer further purified by several reprecipitations from benzene and methanol. The removal of most of the solvent before analysis was done by the frozen benzene technique[4]. The samples were finally dried to constant weight at 56° and a pressure of about 2 mm.

The conversion was measured by drying a known portion of the acid coagulum to constant weight at 80°.

The composition of the polymer samples in terms of percentage of styrene was determined from their iodine numbers according to the method of Kemp and Peters[5] in which per cent styrene $= 100 - (100 \times \text{iodine value}/372.6)$. Results from two runs are shown in Figure 1. The data of Run 20 were obtained from samples taken after reaction periods of three, eight, thirteen, twenty-one, and twenty-four hours, respectively; those of Run 21 were from ten and sixteen hour samples.

FIG. 1.—Variation of styrene content with degree of conversion: ○, run 20; ◑, run 21; ●, theoretical point.

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EMULSION POLYMERIZATION OF DIENE
HYDROCARBONS *

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Less than a century ago Williams obtained isoprene by the thermal decomposition of natural rubber. This discovery was an essential step in a series of researches in several different countries which has culminated in the production of over a million tons of synthetic rubberlike products in a single year. The chemist, like the rubber tree, is able to produce various types of rubber as aqueous emulsions, although the actual processes of manufacture are undoubtedly far different. Liquid butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, and chloroprene have been polymerized to rubberlike materials without the addition of other chemicals, but the chemist and chemical engineer have been more successful in producing uniform products by commercially practical methods since the emulsion processes for polymerization were developed.

This paper is an attempt to summarize the results obtained in investigating the emulsion polymerization of conjugated diene hydrocarbons in these laboratories from 1935–42. During the past four years other commercial and academic laboratories have investigated certain phases of this problem in more detail than is presented in this paper.

Before discussing the properties of the products obtained from specific polymerizable compounds, it seems advisable to consider certain factors, such as purity of reagents, monomer-water ratio, etc., which may have a marked effect on the rate of polymerization or properties of the products.

PURITY OF REAGENTS

The purity of all materials used to prepare the emulsions must be carefully controlled since the addition of almost any compound is likely to accelerate or to retard polymerization or to affect the quality of the product. In preliminary work at least, all monomers should be freshly distilled, preferably at reduced pressure, to minimize polymerization during distillation. The effect of exposure to air and possible formation of peroxides must be considered. Many of these peroxides are not only hazardous, but may have either a favorable or an unfavorable influence on polymerization. It is also advisable to use distilled water in preliminary experiments, since the presence of even minute traces of impurities, such as copper or iron, may alter the polymerization. In one series of experiments the shift from distilled water to tap water available reduced the product yield from 90 to 40 per cent.

While oxygen is generally considered to be a catalyst for polymerization, the presence of an excessive amount of oxygen may retard or actually inhibit

polymerization.   Carbon dioxide has a retarding effect on the polymerization rate in many systems, and results may be influenced by contamination of samples stored in a dry-ice box.

RATIO OF MONOMER TO WATER

The concentration of the monomer in the emulsion may have a marked influence on the rate of polymerization.   For example, the yield obtained by polymerizing a butadiene–methyl methacrylate mixture in sodium oleate emulsion, under otherwise identical conditions and with the ratio of monomers to all components except water the same, increased from 36 to 62 to 85 per cent when the monomer content of the emulsion was increased from 20 to 30 to 45 per cent, respectively.   Although more concentrated emulsions may polymerize faster, their greater viscosity results in poor heat transfer, and control of polymerization at a fixed temperature becomes more difficult.

PREPARATION OF EMULSIONS

Uniformity of initial monomer emulsions is important to obtain reproducible polymerization cycles and uniform quality of polymer.   In small scale laboratory work it is usually sufficient to agitate the polymerizing vessel during polymerization.   Frequently it is advantageous to form the emulsifying agent *in situ*[1] rather than to use a prepared material.   When working with fatty acids, rosins, or long-chain amines, we dissolve the oil-soluble material in the monomer and dissolve the water-soluble alkali or acid in the aqueous phase. A uniform, well-dispersed emulsion is readily obtained when these two solutions are mixed and agitated in the preliminary stages of the polymerization process. Although we have not observed pronounced differences as a result of using a preformed emulsifying agent instead of that formed *in situ*, the micellization of the agent could be different.   Variations might be expected, therefore, in certain polymerization systems.

METHOD OF ADDITION

Experience has shown that misleading results may be obtained by failure to add everything to the polymerization system in the proper sequence.   If the different monomers are mixed for some time before emulsification, there is a possibility of a Diels-Alder type of reaction taking place to an extent sufficient to alter the properties of the product or to reduce the yield.   The addition of a catalyst activator to the aqueous solution too long before its use in the polymerization system may result in a retardation rather than an activation of the polymerization rate.   In investigating the copolymerization[2] of butadiene and methylvinyl ketone, it was discovered that the addition of the ketone to the aqueous solution of soap and catalyst a short time before the butadiene was added resulted in the formation of almost no polymer.   When the two monomers were added simultaneously to the aqueous solution, a good yield of high grade product was obtained.

EMULSIFYING AGENTS

The primary purpose of the emulsifying agent is to assist in the formation of a stable oil-in-water emulsion which does not break during polymerization but gives a latex capable of being readily broken or coagulated after polymerization is completed.   However, it is well known that emulsifying agents not only

serve as such, but also affect the rate of polymerization and the quality of the resulting elastomer. Typical emulsifying agents for use in alkaline systems include the alkali metal and ammonium salts of fat acids, rosin, modified rosins, napththenic acids, alcohol sulfate esters, and various aliphatic and aromatic sulfonic acids. In acidic emulsions the hydrohalides of long-chain amines may be useful. Other nitrogen-containing compounds, such as the quaternary ammonium halides and substituted betaines, have given good results under various conditions.

Mixtures of 75 butadiene–25 styrene were polymerized in the presence of DD thiol (Lorol thiol from C_{12}–C_{14} alcohols) in potassium persulfate–activated systems containing 4 or 5 per cent of some of the more promising emulsifying agents. The following results indicate that various types of emulsifying agents may be used successfully:

Emulsifying agent (%)	pH	Polymerization		
		Temp. (° C)	Time (hrs.)	Product yield[a] (%)
Fatty alcohol sulfate (5)	3	50	12	70
	6	50	12	90
	>10	50	12	95
Aliphatic (average C_{16}) sodium sulfonate (4)	>10	40	20	96
Sulfated methyl oleate (4)	>10	40	20	84
Sodium naphthenate (4)	>10	40	20	93
Sodium oleate (4)	>10	40	17	92

[a] Throughout this paper the term "product yield" is used to denote the yield based on original weight of monomeric material employed without correcting for the emulsifying agent or stabilizer included in the finished elastomer.

Satisfactory emulsions are obtained by using some of the commercially available soaps, such as Ivory and Palmolive, as well as sodium oleate. The merits of the Rubber Reserve soap are well known. Nancy wood rosin soap alone may give interesting polymers but is not very satisfactory for persulfate-activated butadiene systems, owing to the slow rate of polymerization. The rate of polymerization may be greatly increased by hydrogenating the rosin or subjecting it to hydrogen exchange.

Combinations of rosin soaps with fat acid soaps appear to be advantageous when employed in certain preferred polymerization systems. The use of the rosin soap tends to reduce the precoagulation during polymerization, to improve the mill behavior of the polymer, and to result in polymers that are more uniform with respect to tensile properties. The following results, obtained with 75 butadiene–25 styrene mixture, in potassium persulfate–potassium ferricyanide activated systems, indicate that a mixture of 4 per cent oleic acid and 2 per cent Nancy wood rosin gives desirable results:

Oleic acid[a] (%)	Nancy wood rosin (%)	Ratio, rosin: total acid	Total emulsifying agent (%)	Product yield at 40° C for 20 hrs. (%)
0	4	1.0	4	25
4	0	. .	4	93
3	1	0.25	4	9
3	2	0.40	5	90
4	1	0.20	5	95
4	2	0.33	6	97
4	3	0.43	7	93

[a] Commercial red oil was used.

If neither rosin nor fat acid is desired in the finished product, the sulfonic acid type of emulsifying agent may be preferred. Conditions of coagulation may be such as to convert the sulfonic acid to an innocuous insoluble salt or to leave it in a highly soluble form that can be washed out of the polymer.

Some materials that are relatively ineffective as emulsifying agents in preparing the initial emulsion are quite effective as dispersing agents for preventing flocculation of the emulsion during polymerization. An example is the condensation product of a naphthalenesulfonic acid and formaldehyde[3] such as that sold commercially as Daxad 11. The use of such an agent may permit decreasing the percentage of soap required.

CONCENTRATION OF EMULSIFYING AGENT

The rate of polymerization may be markedly influenced by the concentration of the emulsifying agent. For example, monomer conversions of 50–69 per cent have been obtained by polymerizing butadiene for 64 hours at 10° C, using 25 per cent of sodium oleate. Increasing the sodium oleate to 50 per cent has given monomer conversions of 62–76 per cent, depending on the catalyst, in 40 hours. By contrast, when 4 per cent of soap was used, several hundred hours were required for comparable polymer yields.

The effect of variations in concentration of sodium oleate on two different butadiene-styrene systems is shown by the following data; in each case 0.75 part excess sodium hydroxide, 1 part Daxad 11, and 1 part potassium persulfate were used:

Butadiene-styrene ratio	70:30	75:25
Potassium ferricyanide (%)	0	0.15
Thiol (%)	Pinene, 1	DD, 0.75
Hours of polymerization	32 at 40° C	10 at 50° C
Product yield (%)		
4% Na oleate	..	90
6% Na oleate	88	97
8% Na oleate	97	105
10% Na oleate	102	..

EFFECT OF ALKALINITY

The rate of polymerization is influenced also by the pH of the emulsion. The relations between the yield and varying amounts of excess sodium hydroxide for 75 butadiene–25 styrene mixtures polymerized in the presence of
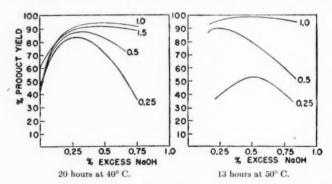
Fig. 1.—Effect of excess sodium hydroxide with varying persulfate on polymerization of 75 butadiene-25 styrene in oleate-rosinate emulsion (numbers on curves refer to per cent potassium persulfate).

varying amounts of potassium persulfate in emulsions containing 4 parts oleic acid, 2 parts rosin, 1 part Daxad 11, 0.15 part potassium ferricyanide, and 1.75 parts pinene thiol are shown in Figure 1.   For each concentration of persulfate, there is a concentration of sodium hydroxide which appears to give the optimum results.

Figure 2 indicates that the rate of polymerization of a 75 butadiene–25 styrene mixture in sulfonated petroleum oil emulsions is influenced by the concentration of the emulsifying agent and the amount of excess caustic in much the same manner as in the fat acid soap systems; but in these cases the optimum rates are obtained with somewhat lower concentrations of excess caustic.   It appears that at least 4 per cent of emulsifying agent is required to give a stable emulsion with a suitable polymerization rate.   The emulsion contained, in addition to the sulfonated petroleum oil, 1 part Daxad 11, 0.75
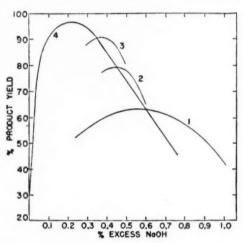
Fig. 2. —Effect of excess sodium hydroxide on polymerization of 75 butadiene-25 styrene in sulfonated petroleum oil emulsions for 20 hours at 40° C (numbers on curves refer to per cent sulfonated petroleum oil).

part DD thiol, 1 part potassium persulfate, and 0.15 part potassium ferricyanide.   The addition of 2 per cent of rosin improves the stability of the emulsion, but, even here, the use of less than 4 per cent of sulfonated hydrocarbon results in an excessively slow polymerization cycle.

CATALYSTS

The use of catalysts or polymerization initiators is essential to obtain suitable polymerization rates.   In practice oxygen-yielding compounds have been found more effective and more adaptable to control than oxygen itself.   Although the term "catalyst" has been applied to such compounds, they are not catalysts in the true sense since they are usually consumed.   Compounds such as benzoyl peroxide or fat acid peroxides, which are soluble in the oil phase, can be used as catalysts but in practice have given less favorable results than the water-soluble types.   Hydrogen peroxide can be used, but salts of per acids such as persulfates and perborates have given more consistently satisfactory results.   The choice of catalyst depends on the other components of the poly-

merization system. In general, persulfates have been favored in the work covered by this report, but some interesting results with *tert*-butyl hydroperoxide also have been obtained.

There is usually an optimum concentration of catalyst, which may vary with the different systems. The following data, obtained by polymerizing a mixture of butadiene and methyl methacrylate for 16 hours at 60° C in alkaline–sodium oleate emulsion catalyzed with ammonium persulfate, indicate that 1 per cent functions as a more effective catalyst than either smaller or larger amounts in this particular system:

Ammonium persulfate (%)	Product yield (%)	Ammonium persulfate (%)	Product yield (%)
0	6	1.0	97
0.25	50	1.5	95
0.5	85	2.0	58

Similar variation in polymerization rates with variations of potassium persulfate is shown by a more complicated butadiene-styrene system in Figure 3.
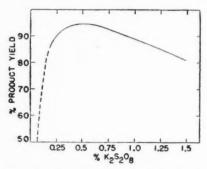
Fig. 3.—Effect of persulfate on polymerization of butadiene-styrene in aliphatic sulfonate emulsion for 18 hours at 40° C.

Butadiene	75	Daxad	1
Styrene	25	DD thiol	0.75
Water	150	$K_3Fe(CN)_6$	0.15
Aliphatic (C_{16}) sulfonate	4	$K_2S_2O_8$	x
Excess NaOH	0.15		

It is possible that the lower yield with higher concentrations of persulfate may have been due to a variation in the pH of the emulsion, caused by the decomposition of the persulfate.

CATALYST ACTIVATORS

The acceleration of polymerization by a primary catalyst such as a persulfate may be greatly increased by the use of a secondary catalyst or activator. As will be discussed later, compounds such as thiols, used as modifying agents, also may affect the polymerization rate. For diene hydrocarbons certain iron and copper complex compounds, such as complex metal cyanides, have been found to be especially effective activators.

Typical data follow which illustrate the favorable influence of potassium ferricyanide on the polymerization rate of a 75 butadiene–25 styrene mixture in a system containing 4 parts oleic acid, 0.75 part excess sodium hydroxide, 0.75 part DD thiol, 1 part Daxad 11, and 1 part potassium persulfate:

Potassium ferricyanide (%)	Product yield at 40° C (%)		Potassium ferricyanide (%)	Product yield at 40° C (%)	
	12 hours	16 hours		12 hours	16 hours
0.005	a	70	0.1	..	91
0.025	a	80	0.15	70	93
0.05	a	90	0.2	74	92

a Low yield of polymer, too soft and tacky to mill.

Figure 4 shows results obtained by polymerizing 75 butadiene–25 styrene in a 33 per cent emulsion containing 5 parts Palmolive soap and 0.5 part DD thiol, with and without excess sodium hydroxide and Daxad 11. The ferricyanide considerably accelerates the polymerization, and in this soap system the addition of 0.15 per cent appears most desirable. Several of these products had acceptable properties even when obtained in essentially 100 per cent product yields.
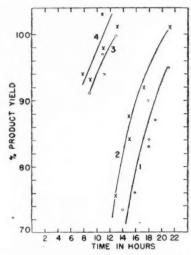
FIG. 4.—Effect of potassium ferricyanide on polymerization of 75 butadiene–25 styrene at 50° C in emulsion containing 5 parts Palmolive soap and 0.5 part DD thiol.

Curves No.	1	2	3	4
$K_2S_2O_8$	0.6	1.25	0.6 or 1.25	0.6 or 1.25
$K_3Fe(CN)_6$	..	..	0.15	0.15
Excess NaOH	..	..	..	0.25
Daxad 11	..	..	..	0.25

Potassium ferrocyanide also has a marked effect on polymerizations activated with *tert*-butyl hydroperoxide (Figure 5). These results indicate that there is an optimum concentration for both potassium ferrocyanide and *tert*-butyl hydroperoxide.

MODIFYING AGENTS

The term "modifying agent" or "regulator" is used to designate compounds which, when present in small proportions during polymerization, markedly increase the plasticity and solubility of the resulting elastomers. They are important tools for improving the processability of the product. Thiols[4], thiuram disulfides[5], xanthic disulfides[6], sulfur[7], selenium[8], substituted phosphines[9], carbon tetrachloride[10], and various nitrogen compounds such as hydrazines[11], amines[12], Schiff bases[13], nitroso compounds[14], and diazoamino compounds[15] have been used to modify diene hydrocarbon polymers and copolymers.
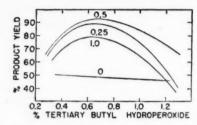
FIG. 5.—Effect of *tert*-butyl hydroperoxide with varying ferrocyanide on polymerization of butadiene-styrene in oleate emulsion for 16 hours at 40° C.   (Curve numbers refer to per cent K₄Fe(CN)₆.3H₂O.)

Butadiene	75
Styrene	25
Water	150
Oleic acid	4
Excess NaOH	0.75
Daxad 11	1
DD thiol	1
tert-Butyl hydroperoxide	*x*
Potassium ferrocyanide	*y*

Thiols as a class are probably the most useful modifying agents, and an elastomer of almost any desired plasticity may be obtained from many different monomers by using the proper concentration of a suitable thiol.   There appears to be a direct relation between the concentration of the thiol and the plasticity of the resulting elastomer.   Unfortunately the more plastic products may yield vulcanizates which are inferior in resilience, tensile strength, tear resistance, and other properties.   Since the effect of thiols of various chain lengths is not identical, a study was made of thiols produced from twenty-one different readily available petroleum oils.   The data in Table I were obtained

TABLE I

EFFECT OF THIOLS MADE FROM HYDROCARBONS ON 75 BUTADIENE-25 STYRENE POLYMERIZATION, WITH 0.75 PER CENT THIOL FOR 20 HOURS AT 40° C

Oil	Average C chain	Product yield (%)	Modification	Stress-strain data		
				Cure (min. at 142° C)	Stress at 300% (lbs. per sq. in.)	Tensile strength (lbs. per sq. in.)	Elongation at break (%)
Dependip	7.6	81	Fair	60	1360	3150	510
Octane	8	85	Fair	45	1410	4120	570
HFVM & P naphtha	9.5	80	Fair	60	1700	3270	450
Oleum spirits	9.8	85	Fair	45	1080	3010	570
Tydol No. 1	10.9	85	Good	45	1070	3420	620
Deobase	10.9	89	Very good	45	1140	2900	540
Perfection kerosene	11	83	Good	60	1480	3270	500
Fortnite LTB	11.1	90	Good	45	1450	2930	465
No. 30 white oil	11.7	94	Very good	45	1160	2760	525
Bayol D	11.8	92	Very good	60	1420	2440	430
Tydol No. 2	12	85	Good	45	1020	3280	620
No. 9 refined	12.1	90	Good	45	1280	3380	540
Control (DDM)	12.5	94	Very good	45	1250	3210	560
Pure No. 1	12.8	93	Very good	45	1220	3410	560
Penn No. 1	13.1	95	Very good	60	1510	3320	500
Penn No. 2	13.3	92	Good	45	2050	3840	440
Penn No. 3	14.1	92	Fair	60	1880	3010	400
No. 40 white	16	92	Fair	45	1330	3590	495
Penn No. 4	18.1	82	Poor	45	2060	3780	435
No. 50 white	19	78	Poor	30	1740	3860	480
No. 70 white	22.5	69	Poor	30	2470	2710	315

by polymerizing mixtures of 75 butadiene–25 styrene in 40 per cent emulsions containing 4 parts oleic acid, 1 part rosin, 0.75 part sodium hydroxide, 1 part potassium persulfate, 1 part Daxad 11, 0.15 part potassium ferricyanide, and 0.75 part of the thiol (active ingredients). One hundred parts of the elastomers were compounded with 50 parts MPC black, 2 parts stearic acid, 2 parts sulfur, 5 parts zinc oxide, and 1.25 parts 2-mercaptothiazoline.

The Williams plasticity numbers[16] of elastomers modified with different samples of thiols are plotted against the number of carbon atoms in the thiol chain in Figure 6. Although experimental variations and inequalities in yield make it difficult to draw exact conclusions, primary thiols containing 11 to 14 carbon atoms appear to be most effective in the persulfate-catalyzed fat acid soap systems used.
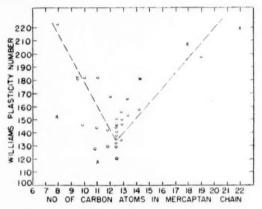
Fig. 6.—Effect of chain length of thiol on plasticity of copolymer from 75 butadiene–25 styrene mixture with 0.75 part mercaptan (100 per cent basis). 20 hours at 40° C.

○ = product yield of 85 to 95%.
✕ = product yield of 70 to 85%.

Although aromatic thiols were not especially effective as modifying agents, interesting results were obtained with certain cyclic thiols, such as pinene thiol and menthene thiol, and with branched-chain thiols, such as Sharples 3B thiol[17]. Table II gives results obtained with a ferricyanide-activated 4 per

TABLE II

COMPARISON OF PINENE AND DD THIOLS

Thiol (percentage)	Polymerization time (hrs.)	Product yield (%)	Williams plasticity-recovery	Stress-strain data[a]		
				Stress at 300% (lbs. per sq. in.)	Tensile strength (lbs. per sq. in.)	Elongation at break (%)
None	24	60	337–161	2550	3580	380
None	49	93	369–138	. .	1845	190
0.25 DD	24	88	271–180	2640	3465	350
0.75 DD	20	95	134–173	1420	3180	500
1.5 DD	20	96	82–5	995	2215	540
1.0 pinene	22	92	230–220	1620	3610	500
2.0 pinene	20	93	156–145	1280	3210	530
4.0 pinene	20	98	107–100	850	2215	380

[a] On 2-MT (2-mercaptothiazoline) tread stocks cured 45 minutes at 142° C.

cent sodium oleate emulsion of a 75 butadiene–25 styrene mixture polymerized at 40° C. In each case the tensile data show the unfavorable influence of an excess of thiol.

Table III shows results obtained in comparing DD, menthene, and 3B thiol in 36 per cent emulsions containing 5 parts Palmolive soap and 0.6 part potassium persulfate, and polymerized at 50° C.

TABLE III
COMPARISON OF DD, MENTHENE, AND 3B THIOLS

Thiol (percentage)	Polymerization time (hrs.)	Product yield (%)	Williams plasticity-recovery	Stress-strain data[a]		
				Stress at 300% (lbs. per sq. in.)	Tensile strength (lbs. per sq. in.)	Elongation at break (%)
0.5 DD	15	86	106–24	1510	3130	490
0.5 DD	18	90	135–107	1670	3580	490
0.5 DD	21	95	144–116	1760	3090	430
0.3 menthene	19	76	102–25	1420	2980	500
0.3 menthene	21	93	130–104	2185	2840	350
0.4 menthene	19	84	90–12	1450	2640	450
0.1 3B	99	56	133–144	1645	3380	470
0.2 3B	22	71	96–11	1620	2900	440
0.3 3B	19	74	60–9	1450	2840	490
0.3 3B	22	78	65–9	1645	3065	460

[a] On tread stocks cured 45 minutes at 142° C.

The thiols not only affect the plasticity of the product but also the rate of polymerization. Figure 7 shows data obtained with 40 per cent emulsions containing 4 parts oleic acid, 0.75 part excess sodium hydroxide, 1 part Daxad
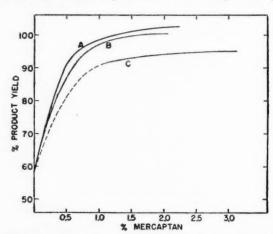
FIG. 7.—Effect of thiol concentration on polymerization of 75 butadiene–25 styrene in oleate emulsion for 20 hours at 40° C.

A, DD thiol; B, No. 30 white oil thiol; C, pinene thiol.

11, 1 part potassium persulfate, and 0.15 part potassium ferricyanide. No attempt was made to exclude air from this system, and whether the thiol affects induction period or actual polymerization rate remains to be determined.

It was considered that a combination of thiols might be even more suitable than a single thiol. Thus, it might be possible to combine the greater modifying action of 3B thiol with the accelerating action of DD thiol. The results obtained (Figure 8) indicate that the single and mixed thiols give distinct sets of nearly parallel curves; although the mixed thiols have a greater influence on plasticity at low yields, the single thiols are more effective in increasing the plasticity at higher yields. It is possible that the acceleration of polymerization with mixed thiols accounts for these results. If the rate of diffusion of the modifier to the point where polymerization is in progress is involved, acceleration of polymerization might explain the anomaly of less modifier being more effective under certain conditions.
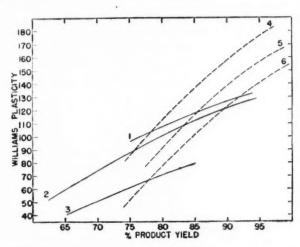
FIG. 8.—Effect of yield on plasticity of compounds modified with combinations of thiols.

Curve No.	1	2	3	4	5	6
DD (%)	..	0.5	..	0.05	0.05	0.05
Menthene (%)	0.3	..	..	0.3	..	0.4
3B (%)	..	..	0.3	..	0.3	..

A study of the mechanism of the action of modifying agents offers a promising field for academic research. Some of these modifying agents may function by terminating polymer chain growth or introducing easily rupturable linkages and, thereby, result in products of lower molecular weight. Other modifying agents may act by preventing cross-linking or by interfering with cyclization. The utility of a given compound as a modifying agent depends on the nature of the monomer, the emulsifying agent, the pH of the emulsion, or the method of catalysis.

TEMPERATURE OF POLYMERIZATION

The rate of polymerization can be increased by raising the temperature, but our general experience has shown that the quality of the elastomer is improved by polymerizing at lower temperatures. In some cases freeze resistance is increased by raising the temperature of polymerization, but processability, tensile strength, and elasticity are generally improved by polymerization at lower temperatures.

STABILIZERS

Elastomers made from diene hydrocarbons must be protected from oxidation during milling and processing. For this reason it is advisable to add an antioxidant, preferably in the form of an aqueous dispersion, to the latex when the optimum yield is reached[18]. Such a dispersion may be prepared from any antioxidant by grinding with a suitable dispersing agent or emulsifying a solution of the antioxidant in an inert solvent. The antioxidants may serve to terminate polymerization, but in certain cases other agents or inhibitors are also added.

COAGULATION

A suitable coagulation process should be complete, yield a readily washable coagulum, and have no adverse effect on the properties of the product. Coagulation of most of the emulsions discussed in this report may be brought about by adding salts of bi- or trivalent metals such as barium, magnesium, or aluminum, or by the addition of sodium chloride brine or acidified brine, or by cooling or heating. An acidic coagulant is advantageous for coagulation of soap latices since it converts the soap to free fat acid or rosin and a highly soluble salt. When practical, cooling or heating are preferred methods of coagulation because they involve no contamination of the finished product with coagulant. For example, Neoprene latices containing sodium rosinate and Daxad 11 are acidified with sufficient acetic acid to precipitate the rosin and are then coagulated by freezing on a rotating drum. The resulting film is washed with water to remove sodium acetate. In this laboratory an acidic sodium chloride brine is commonly used to coagulate butadiene latices made with fatty acid or rosin soaps.

YIELD

Every manufacturer of elastomers knows that the properties of his product are greatly affected by the yield at which the product is isolated. However, it is frequently possible, by the proper use of modifiers and by polymerizing at sufficiently low temperature, to polymerize to a yield of 90 per cent or better and still obtain a good-processing polymer which yields suitable vulcanizates. The maximum yield obtainable without adversely affecting the product is influenced not only by the character of the modifying agents added to the system, but also by the nature and amount of impurities in the polymerizables since impurities are frequently negative modifiers.

LABORATORY PROCEDURE

Glass equipment appears to be most satisfactory for use in laboratory polymerization. With materials having boiling points appreciably above the temperature of polymerization, it is possible to carry out the emulsion polymerization at atmospheric pressure. Since butadiene boils at $-5°$ C, it is necessary in this case to use closed systems. It has been found satisfactory to use thick-walled Pyrex tubes (approximately 3×40 cm.) enclosed in holders made from perforated metal tubes and rotated end to end (35 r.p.m.) in a water bath at the desired temperature. These tubes are closed with Neoprene stoppers which have been treated with caustic solution to remove extractable material. In filling the tubes, the water and water-soluble ingredients are placed in the tube, and the mixture is frozen by placing the tube in an acetone–solid carbon dioxide bath. Liquid butadiene and butadiene-soluble materials

are then weighed into the tube, and the tubes are sealed and warmed to the desired temperature.

After the aqueous phase has been thawed, the tube can be shaken rapidly, if necessary, to form the emulsion, but usually simple rotation in the water bath is sufficient. If, on removal from the water bath, the tube is suspected of containing appreciable amounts of butadiene, it is cooled to about 0° C before being opened. After coagulation, the polymers are washed on a 6 × 2 inch (15.2 × 5.1 cm.) wash mill with one corrugated roll. The washed elastomer is dried first on a corrugated mill and finally on a smooth 6 × 2 inch mill with differential speed rolls.

The samples are compounded on these small mills and cured at conventional temperatures and pressures in small presses. The apparatus used in determining the tensile properties of these samples was described by Williams and Sturgis[19].

Since elastomers containing butadiene are notoriously inferior in gum stocks, black stocks were used in compounding. The usual cure was 30 minutes at 153° C, and the formula generally employed was:

Elastomer	100	Sulfur	2
Phenyl-*1*-naphthylamine	2	Mercaptobenzothiazole	1
MPC black	50	Zinc oxide	5
Stearic acid	2		

In some recent work more active accelerators, such as 2-mercaptothiazoline, were employed. With some samples tensile strength measurements were made at temperatures ranging from −40° to +100° C.

Resistance to swelling in solvents is usually determined by weighing the sample in air and in water at room temperature before and after emersion in the solvent.

Several more practical methods for the determination of freeze resistance have been developed since this work was started, but valuable preliminary information was obtained by using a modification of the T-50 method described by Gibbons, Gerke, and Tingey[20]. In this modification the temperature at which each 10 per cent retraction occurred is reported; that is, a T-10 of −40° C means that a sample stretched 240 per cent of its original length when frozen at −70° C and then released to allow free retraction, retracted 10 per cent of the elongation when warmed to −40° C. The T-20 is the temperature at which it retracted 20 per cent, etc.

The hardness (Shore durometer Type A) and the Schopper rebound were measured with a pile of three slabs.

Elastomers which gave interesting results in those preliminary tests were evaluated further by conventional rubber testing methods.

ELASTOMERS FROM BUTADIENES

The sodium-catalyzed polymerization of 1,3-butadiene was used extensively in formulating the numbered Bunas in Germany and SKA and SKB in Russia[21]. Less attention has been given to the emulsion polymerization of butadiene alone, and it is generally assumed that the presence of another polymerizable compound is essential to prevent excessive cross-linkage or to give the preferred 1,4 addition and obtain the best products.

The present commercial processes do involve the use of another polymerizable compound with the butadiene, but it is possible to improve the elastomers obtained from butadiene alone by suitable emulsion technique. How-

ever, to obtain high-quality butadiene polymers in emulsion, it is necessary to polymerize at lower temperatures than are commonly used commercially. The following data show the results of tests on straight butadiene polymers made in a 4 per cent sodium oleate emulsion containing persulfate and octanethiol, and polymerized at 10° C:

Ammonium persulfate (%)	Octanethiol (%)	Product yield (%)	Stress at 300% (lbs. per sq. in.)	Tensile strength (lbs. per sq. in.)	Elongation at break (%)
1	2	38	820	1500	420
		48	630	2940	640
		66	850	2180	460
		80	. .	1450	250
0.5	1	30	480	1900	620
		40	820	2090	460
		52	1130	1600	350

In both systems the product isolated at an intermediate yield is superior to that at either the highest or the lowest yield. As Figure 9 shows, the polymerization rate is far slower than that used in commercial systems, but it is
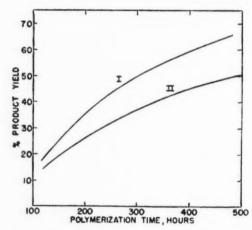
Fig. 9.—Polymerization rate of butadiene in oleate emulsion at 10° C in presence of octanethiol and ammonium persulfate.

I. 1% ammonium persulfate, 2% octanethiol.
II. 0.5% ammonium persulfate, 1% octanethiol.

possible to modify the system so as to obtain faster polymerization rates. For example, a 92 per cent yield was obtained in 64 hours at 10° C by using a system containing 25 parts oleic acid, 0.5 part excess sodium hydroxide, 1 part Daxad 11, 0.5 part sodium persulfate, 1 part DD thiol, 4 parts methanol, 0.1 part potassium ferrocyanide, and 200 parts water per 100 parts butadiene. The product, compounded in a typical channel black stock, gave a vulcanizate having a tensile strength of 2,500 pounds per square inch and an elongation at break of 650 per cent. This shows that high yields of good quality butadiene polymers are possible.

Isoprene gave reasonably good polymers, although in general they were inferior to those from butadiene. A 90 per cent yield of isoprene polymer was

obtained at 30° C, and it gave vulcanizates with a tensile strength of 1,950 pounds per square inch at 480 per cent elongation. Practical road tests indicate that, in spite of these comparatively poor tensile properties, a tread of polyisoprene would give more than half as much service as a Grade A rubber tread.

2,3-Dimethyl-1,3-butadiene gives better milling elastomers than either butadiene or isoprene, but loggy vulcanizates which have a greater tendency to freeze. They have good tensile strength, as indicated by the following data obtained with polymers formed in an alkaline oleate emulsion containing persulfate and cured 30 minutes at 153° C:

| Polymerization | | Product yield (%) | Stress at 300% (lbs. per sq. in.) | Tensile strength (lbs. per sq. in.) | Elongation at break (%) |
Temp. (° C)	Time (hrs.)				
100	4	50	1410	2720	460
60	65	100	1900	2900	390
50	17	72	1810	3030	420
30	90	72	2040	2660	350

The polymerization of mixtures of 1,3-butadiene and 2,3-dimethyl-1,3-butadiene produces elastomers which are superior in stress-strain properties to those obtained from butadiene alone under similar conditions:

| Butadiene (%) | Polymerization | | Product yield (%) | Stress at 300% (lbs. per sq. in.) | Tensile strength (lbs. per sq. in.) | Elongation at break (%) |
	Temp. (° C)	Time (hrs.)				
10	50	67	105	1810	2770	390
10	30	18	76	1610	2800	430
20	30	18	81	1700	2940	430
30	30	18	82	1920	2580	350
60	30	90	88	1410	2550	430
60	50	16	86	1470	1900	350

The freeze resistance of these dimethylbutadiene-butadiene copolymers, as indicated by retraction during gradual warming in the T-50 apparatus, shows a definite improvement as the butadiene content is increased. This is shown by the curves of Figure 10.
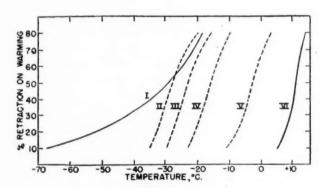
Fig. 10.— Freeze resistance of butadiene-dimethylbutadiene elastomers.

Curve No.	I	II	III	IV	V	VI
1,3-Butadiene (%)	100	40	30	20	10	..
2,3-Dimethyl-1,3-butadiene(%)	..	60	70	80	90	100

Even more freeze-resistant elastomers can be obtained by polymerizing mixtures of isoprene and butadiene (Figure 11). Tensile data follow on elastomers cured 30 minutes at 153° C:

Butadiene (%)	Isoprene (%)	Polymerization time at 35° C (hrs.)	Product yield (%)	Tensile strength (lbs. per sq. in.)	Elongation at break (%)
0	100	64	35	..	..
0	100	112	69	1330	410
50	50	64	54	1580	540
50	50	112	87	1300	230
75	25	64	61	1840	490
100	0	64	67	1600	430

These results were obtained with a system containing 4 parts oleic acid, 1.5 parts ammonia, 1 part Daxad 11, 1 part ammonium persulfate, and 2 parts octanethiol. Milled blends of the separately formed polymers from butadiene, isoprene, or dimethylbutadiene do not show the superiority in freeze resistance of the corresponding copolymers. This difference in freeze resistance is believed to be an indication of the formation of polymers which contain, in a single chain, units of both polymerizing monomers.
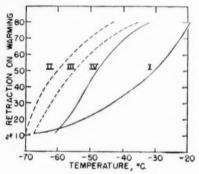
FIG. 11.—Freeze resistance of butadiene-isoprene elastomers.

Curve No.	I	II	III	IV
1,3-Butadiene (%)	100	75	50	..
Isoprene (%)	..	25	50	100

This work has served to demonstrate that high quality polymers can be made from diene hydrocarbons alone by polymerization in emulsion, and that some advantage may be expected from copolymerization of different hydrocarbons. The emulsion polymerization of these diene hydrocarbons is worthy of more detailed investigation, and the development of the proper system may result in an elastomer superior to GR-S for general use.

COPOLYMERS OF BUTADIENE AND VINYL COMPOUNDS

Although good elastomers can be made from butadiene alone, thus far it has been easier to make a good quality product from mixtures of butadiene with other polymerizable compounds. The first work was that of Tschunkur, Meisenburg, and Bock, using styrene and vinyl naphthalene[22]. Many other types of compounds copolymerizable with butadiene were studied later by various investigators, but it is not possible to give here a complete bibliography

of the extensive literature on the subject. In general, the second polymerizable components are vinyl compounds which contain an activating group such as a second vinyl, a nitrile[23], a carboxyl[24], or a phenyl group. Activation may also be accomplished by unsymmetrical substitution of two or more halogen atoms on a double-bonded carbon[25]. Many of these vinyl compounds have been investigated, but only a few have given sufficiently attractive products or are sufficiently available commercially to be considered for the manufacture of synthetic rubbers. Table IV summarizes the properties of butadiene copolymers with vinyl compounds having different activating groups.

In this series of tests the second monomer was used on an equimolar rather than an equal weight basis, the ratio being 4.3 moles of butadiene per mole of the second vinyl compound. The mixed monomers were polymerized in an emulsion containing 5 parts oleic acid, 1.06 parts sodium hydroxide, 1 part Daxad 11, 1 part ammonium persulfate, 0.5 parts octanethiol, and 116 parts water. Comparison with the results obtained on butadiene alone shows that the addition of the second monomer increases the rate of polymerization in all cases. When the second monomer contains a nitrile group, the rate is further increased by the introduction of alkyl groups.

The kerosene resistance is increased by the presence of chlorine or, especially, nitrile radicals. The introduction of additional alkyl groups tends to decrease the kerosene resistance, and the greater the chain length of the alkyl group, the greater the loss in kerosene resistance.

The introduction of a methyl group decreases the freeze resistance, but the elastomers containing the butyl group are more freeze-resistant than those containing the methyl group.

The compounding formula was as follows: copolymer 100, phenyl-β-naphthylamine 2, stearic acid 2, zinc oxide 5, MPC black 50, sulfur 2, and mercaptobenzothiazole 1.

Table V summarizes data pertaining to the polymerization of mixtures of butadiene with a number of other polymerizable compounds. In testing a new compound, the general procedure was to form a 40 per cent emulsion of a mixture of 70 parts butadiene and 30 parts of second component in an alkaline sodium oleate system with a suitable catalyst, usually a persulfate, and to agitate the emulsion at 30° or 40° C for 65 hours. The emulsion was then treated with an antioxidant and coagulated. The coagulum was washed on a mill with one corrugated roll and milled to constant weight. In some cases, indicated by f, an acid system was used with C-cetylbetaine as emulsifying agent. Many of these experiments were carried out before the present modifiers or catalyst activators were developed. The products, therefore, do not necessarily represent the best that can be obtained from the particular compounds.

The second monomer is considered to have inhibited polymerization when the product yield was 25 per cent of less of that which would have been obtained from the same amount of butadiene alone. Product yields 75–110 per cent of that to be expected from the butadiene are considered normal; lower yields indicate retardation, and higher yields acceleration. In all cases where polymerization was accelerated, copolymers are believed to have been formed. When possible, this was confirmed by determination of a characteristic element such as chlorine or nitrogen. Some combinations with normal or even retarded polymerization rates gave products which contain appreciable amounts of a second monomer.

TABLE IV

PROPERTIES OF BUTADIENE COPOLYMERS WITH VARIOUS MONOMERS
(Structure is $CH_2{=}CRR_1$)

	No second monomer	Acrylonitrile	Methacrylonitrile	Methyl methacrylate	Butyl methacrylate	Methyl α-chloracrylate	Styrene	α-Methylstyrene
R group		H	CH_3	CH_3	CH_3	Cl	H	CH_3
R_1 group		CN	CN	CO_2CH_3	$CO_2C_4H_9$	CO_2CH_3	C_6H_5	C_6H_5
2nd monomer (% by wt.)		18.6	22.4	30	38	34	30.8	33.6
Polymerization data								
Hours at 30° C	65	65	40	65	48	50	88	90
Product yield (%)	55	88	100	93	90	87	83	85
Stress-strain data (cured 30 min. at 141° C)								
Tested at 25° C								
Stress at 300% (lbs. per sq. in.)	900		1380	740	620	1900	650	350
Tensile (lbs. per sq. in.)	2320	2000–2500	2970	2720	2900	2290	3220	2410
Elongation at break (%)	470	400–500	450	600	650	340	650	800
Tested at 70° C								
Tensile (lbs. per sq. in.)	850	1160	1030	1330	1470	650	2010	1700
Elongation at break (%)	250	150	260	470	580	200	620	860
Kerosene absorption (48 hrs. at 100° C)								
Volume increase (%)	>200	42	62	135	203	64	150	195
Freeze resistance								
T-10, ° C	-65	-40	-33	-46	-55	-12	-49	-47
T-50, ° C	-34	-30	-23	-37	-46	0	-41	-38
T-80, ° C	-21	-23	-11	-26	-36	+6	-32	-29

TABLE V

ELASTOMERS FROM BUTADIENE WITH VINYL COMPOUNDS

Second monomer	Polymeri-zation rate[a]	Mill appearance[b]	Tensile strength[c]	Elonga-tion[d]
Acyclic monoenes				
1,1-Dichloroethylene	Acc[e]	Fair	Good	Good
1-Bromo-1-chloroethylene	Norm[e]	Good	Poor	VG
1-Fluoro-1-chloroethylene	Inh	Soft		
cis-1,2-Dichloroethylene	Ret	Tough	Poor	Fair
trans-1,2-Dichloroethylene	Ret	Tough	Fair	Good
1,1,2-Trichloroethylene	Norm[e]	Tough	Poor	Poor
1,1,2-Trifluoro-2-chloroethylene	Ret[e]	Coherent	Fair	Fair
1,1,2,2-Tetrachloroethylene	Ret	Tough	Poor	Fair
2-Chloro-1-propene	Ret	Thready	Fair	VG
3-Chloro-1-propene	Ret	Coherent	Fair	VG
2-Methyl-3-chloro-1-propene	Ret	Soft		
1,1-Dichloro-2-methyl-1-propene	Norm[e]	Flaky	Fair	Fair
1,1,3-Trichloro-2-methyl-1-propene	Ret	Sticky	. .	. .
2,4,4-Trimethyl-2-pentene	Norm	Poor	Poor	Poor
Acyclic dienes				
1-Methyl-1,3-pentadiene	Norm	Good	Poor	VG
2-Methyl-1,3-butadiene	Norm	Good	Fair	VG
2,3-Dimethyl-1,3-butadiene	Acc[e]	Good	Good	Good
1-Chloro-1,3-butadiene	Ret[e]	Crumbly		
2-Chloro-1,3-butadiene	Acc[e]	Fair	Fair	Fair
2-Fluoro-1,3-butadiene	Acc[e]	Poor	Poor	Fair
1-Chloro-2-methyl-1,3-butadiene	Inh			
2-Chloro-3-methyl-1,3-butadiene	Acc[e]	Flaky	Fair	Poor
3-Chloro-2,4-heptadiene	Norm	Fair	Poor	VG
2,3-Dichloro-1,3-butadiene	Inh	. .	. .	. .
1,2,4-Trichloro-1,3-butadiene	Acc[e]	Good	Poor	Poor
1,1,2,3,4-Pentachlor-1,3-butadiene[f]	Ret	. .	Poor	Poor
2-Methyl-1,3-pentadiene	Acc[e]	Good	Fair	Good
3-Chloro-2,5-dimethyl-1,5-hexadiene	Inh	. .	. .	. .
1,3-Dichloro-2,4-hexadiene	Inh	. .	. .	. .
3-Chloro-1,3,4,5-hexatetraene	Inh	. .	. .	. .
5,6-Dichlorohexa-1-en-3-yne	Norm[e]	Good	. .	. .
3,5,6-Trichloro-1,3-hexadiene	Acc[e]	Good	Fair	Fair
2,5-Dimethyl-1,3,5-hexatriene	Inh	Soft	Poor	Fair
Acyclic hydroxy compounds				
Allyl alcohol	Inh	. .	. .	. .
2-Chloro-2-propen-1-ol	Inh	Slime	. .	. .
1-Hydroxy-3-chloro-2,4-hexadiene	Inh	. .	. .	. .
Dimethylvinylethynylcarbinol	Acc[e]	VG	VG	Good
2-Ethoxy-1-butene	Inh	. .	. .	. .
3-Methoxy-2-chloro-1-propene	Ret[e]	Crumbly	Good	VG
3-Methoxy-2-methyl-1,1-dichloro-1-propene	Inh	. .	. .	. .
1-Divinyl ether	Ret	Tender	Poor	Poor
2-Chlorallyl ether	Ret[e]	Fair	Poor	Poor
Isobutylvinyl ether[f]	Ret	Soft	Poor	Good
2-Methylamylvinyl ether[f]	Ret	. .	Poor	Fair
Divinyl sulfide	Inh	. .	. .	. .
1-Mercapto-3-chloro-2,4-hexadiene	Inh	. .	. .	. .
Tetramethallyl silicate[f]	Norm	Poor	Poor	Poor
Methylglycol vinyl ether[f]	Inh	Poor	Poor	Poor
Diethyldiethoxyethylene[f]	Inh	. .	. .	. .
2,3-Diethylthio-1,3-butadiene	Inh	. .	. .	. .

TABLE V—*Continued*

ELASTOMERS FROM BUTADIENE WITH VINYL COMPOUNDS

Second monomer	Polymeri-zation rate[a]	Mill appearance[b]	Tensile strength[c]	Elonga-tion[d]
Oxo compounds				
Chloroacetone[f]	Inh	. .	. .	. .
Crotonaldehyde	Inh	. .	. .	. .
α-Chlorocrotonaldehyde	Inh	. .	. .	. .
1-Buten-3-one (methylvinyl ketone)	Acc[e]	Good	VG	VG
2-Chloro-1-butan-3-one	Norm[e]	Crumbly	Poor	Poor
Mesityl oxide	Inh	. .	. .	. .
Phorone	Ret	Tender	Poor	Poor
Divinylformal	Ret	. .	Poor	Fair
1,1-Diethoxy-2-propene	Ret	Fair	Poor	VG
Dichlorovinylethyl ether[f]	Ret	Soft	Poor	Fair
Biacetyl	Inh	. .	. .	. .
Hexyl ketone dimer[f]	Norm	Poor	Poor	Poor
Monocarboxylic acids				
Acrylonitrile	Acc[e]	Good	VG	Good
Methacrylonitrile	Acc[e]	Coherent	Good	Good
α-Chloroacrylonitrile	Acc[e]	Dry	VG	Poor
α,β-Dichloroacrylonitrile	Acc[e]	Good	Good	Poor
3-Cyano-1-propene[f]	Inh	Sirupy	. .	. .
1-Cyano-2-butene	Inh	. .	. .	. .
2-Cyano-1-chloro-1-propene[f]	Inh	Sirupy	. .	. .
2-Cyano-3-chloro-1-propene[f]	Inh	. .	. .	. .
1-Cyano-3-chloro-1-propene	Inh	Soft	. .	. .
1-Cyano-2-methyl-1-propene	Inh	Powdery	. .	. .
2-Cyano-4-methyl-1,3-pentadiene	Inh	. .	. .	. .
1-Cyano-1,3-butadiene	Norm	Poor	Good	Fair
2-Cyano-1,3-butadiene[f]	Acc	Poor	Poor	Poor
1-Acetoxy-1,3-butadiene[f]	Inh	. .	. .	. .
2-Acetoxy-1,3-butadiene	Ret	Gummy		
1-Acetoxy-3-chloro-2,4-hexadiene	Acc[e]	Good	Fair	Good
1,1-Dichloro-2-methyl-3-acetoxy-1-propene	Ret	Crumbly	Fair	Good
Vinyl formate	Inh	. .	. .	. .
Vinyl acetate	Inh	. .	. .	. .
Vinyl chloroacetate[f]	Inh	. .	. .	. .
Methyl methacrylate	Acc[e]	Good	VG	VG
Ethyl methacrylate	Acc[e]	Good	Good	Fair
n-Propyl methacrylate	Acc[e]	Good	Good	Good
n-Butyl methacrylate	Acc[e]	Good	Good	Good
Butyl methacrylate	Acc[e]	Good	Good	Good
n-Octyl methacrylate	Acc[e]	Tender	Poor	Poor
Vinyl methacrylate	Acc[e]	Good	Poor	Poor
Allyl methacrylate	Acc[e]	Good	Poor	Poor
Methallyl methacrylate	Acc[e]	Dry	Poor	Poor
3-Chloro-2-butenyl methacrylate	Norm[e]	Good	Poor	Poor
2-Nitropropyl methacrylate	Inh	. .	. .	. .
2-Nitro-2-methylpropyl methacry-late[f]	Acc[e]	Good	VG	VG
2-Nitrobutyl methacrylate	Inh	. .	. .	. .
Ethyleneglycol monomethacrylate	Inh	. .	. .	. .
Methoxymethyl methacrylate	Acc[e]	Good	Fair	Fair
Ethyl thiomethacrylate[f]	Acc[e]	Good	Poor	VG
Polycarboxylic acids				
Dimethyl fumarate[f]	Acc[e]	Good	Good	VG
Diisobutyl fumarate	Acc[e]	Tacky	Poor	Good
Diallyl fumarate	Acc[e]	Crumbly	Poor	Poor

TABLE V—*Continued*

ELASTOMERS FROM BUTADIENE WITH VINYL COMPOUNDS

Second monomer	Polymeri-zation rate[a]	Mill appearance[b]	Tensile strength[c]	Elonga-tion[d]
Polycarboxylic acids—*Continued*				
Dimethallyl fumarate	Acc[e]	Crumbly	. .	. .
Di(3-chloro-2-butenyl) fumarate	Acc[e]	Flaky	Poor	Poor
1,2-Dicyanoethylene	Acc[e]	Crumbly	Good	Poor
2-Methyl-2-nitropropyl fumarate[f]	Acc[e]	Fair	Good	Good
Dimethyl maleate[f]	Ret	Soft	. .	. .
Dimethallyl maleate	Acc[e]	Crumbly	. .	. .
Diethyl methylene maleate[f]	Ret	Good	Fair	VG
Diisobutyl maleate	Acc[e]	Fair	Poor	Poor
Ethyl cyanoacetate	Inh		. .	. .
α-Cyanosorbic acid[f]	Ret	Resinous	.	. .
Methyl α-cyanosorbate[f]	Inh	. .		
2-Methyl-2-nitropropyl maleate[f]	Acc[e]	. .	Fair	Poor
Di-2-nitrobutyl fumarate[f]	Inh	. .	. .	
Hydroxy carboxylic acids				
Diallyl carbonate[f]	Norm	Poor	Poor	Poor
Dimethallyl carbonate[f]	Ret		Poor	Poor
Acrolein cyanohydrin acetate	Inh	. .	. .	
3-Cyano-3-acetoxy-1-butene[f]	Ret	Good	Poor	VG
Cyanomethyl methacrylate	Acc[e]	Crumbly	Good	Fair
β-Cyanoethyl methacrylate[f]	Acc[e]	Poor	Poor	Poor
Methacryl isothiocyanate[f]	Inh	. .	. .	
Methacrylurea	Acc[e]	Crumbly	Fair	Poor
Diethoxymethylurea[f]	Norm	Poor	Poor	Poor
Vinyl thiolacetate	Ret[e]	Good	Fair	Good
Dimethyllylmethallyloxy succinate[f]	Ret	Poor	Poor	Poor
Amines				
N-Allyl maleic half-amide[f]	Inh	. .	. .	
Monomethacrylurea	Norm[e]	Waxy	Good	Poor
N-Dimethylcrotonamide	Ret[e]	Good	. .	. .
Dimethallylamine[f]	Acc	Poor	Poor	Good
Methacryl dimethylamide	Inh	Soft	. .	. .
N-Methyl maleic monoamide	Inh	. .	. .	
N-Butyl maleic monoamide	Ret	Soft	. .	
N-Methyl methacrylamide[f]	Norm	Poor	Poor	Poor
N-Stearyl methacrylamide[f]	Acc[e]	Poor	Poor	Poor
Methallyl isothiocyanate	Inh	. .	. .	. .
Dimethylamine hexylmethacrylamide	Inh	. .	. .	. .
N-(β-Dimethyl aminoethyl) meth-acrylamide	Acc[e]	Poor	Poor	Poor
Dimethylaminoethyl metacrylate[f]	Acc[e]	Good	Poor	Poor
Diethylaminoethyl methacrylate[f]	Acc[e]	. .	Fair	Poor
2-Cyanoisopropyl methacrylamide[f]	Inh	. .	. .	. .
2-Propene phosphonic bisdimethyl-amide	Acc	Flaky	Poor	Poor
Isocyclic compounds				
Methylenecyclohexane	Ret	Good	Poor	Good
β-Pinene	Norm	Tender	Poor	Good
Dipentene	Norm	Fair	Poor	Poor
Cyclopentadiene[f]	Norm	Poor	Poor	Poor
Styrene	Acc[e]	Fair	VG	VG
p-Methylstyrene	Norm[e]	Coherent	VG	VG
α-Methylstyrene	Acc[e]	Fair	VG	VG
p-Methyl-α-methylstyrene	Acc[e]	Fair	VG	VG
α-Chlorostyrene	Acc[e]	Dry	Poor	Good
2,5-Dichlorostyrene	Acc[e]	Good	VG	VG

TABLE V—*Continued*

ELASTOMERS FROM BUTADIENE WITH VINYL COMPOUNDS

Second monomer	Polymeri- zation rate[a]	Mill appearance[b]	Tensile strength[c]	Elonga- tion[d]
Isocyclic compounds—*Continued*				
β-Nitrostyrene[f]	Inh	..	..	..
3-Methyl-β-nitrostyrene[f]	Inh	..	..	..
3-β-Dinitrostyrene[f]	Inh	..	..	..
m-Nitrostyrene[f]	Inh	..	..	..
m-Chloro-β-nitrostyrene[f]	Inh	..	..	..
β-Nitro-β-methylstyrene	Inh	..	..	..
1-Phenyl-1,3-butadiene[f]	Acc[e]	Crumbly	..	..
Dicyclopentadiene	Ret	Good	Fair	VG
2,3-Diphenyl-1,3-butadiene	Acc[e]	Good	Good	VG
2,3-Di(p-fluorophenyl)-1,3-butadiene	Norm[e]	Good	VG	VG
Isocyclic hydroxy compounds				
α-Ethoxystyrene	Inh	..	..	..
Cinnamyl alcohol	Inh	..	..	..
p-Methoxy-β-nitrostyrene	Inh	..	..	..
Cyclohexyl methacrylate	Acc[a]	Good	Good	Good
Pentachlorophenyl methacrylate	Inh	..	..	..
Isocyclic oxo compounds				
β-Carbone	Inh	Sticky	..	..
1-Phenyl-1-buten-3-one[f]	Acc[e]	Good	VG	Good
1,3-Diphenyl-1-propen-3-one[f]	Acc[e]	Good	Good	Fair
1-Phenyl-5-chloro-1-penten-3-one	Inh	..	..	..
1,5-Diphenyl-1,4-pentadien-3-one	Acc[e]	Fair	Good	Good
1-Phenyl-1,3-hexadien-5-one	Inh	..	..	..
1-Phenyl-5-methyl-1,4-hexadien-3-one	Acc[e]	Good	Fair	Fair
Cinnamic aldehyde–methylamine	Inh	..	..	..
1-(p-Nitrophenyl)-1-buten-3-one[f]	Inh	..	..	..
1,4-Diphenyl-2-butene-1,4-dione	Acc[e]	Crumbly	Fair	Fair
Isocyclic carboxylic acids				
α-Cyanostyrene	Ret	Waxy- brittle	..	..
β-Cyanostyrene	Acc[e]	..	Fair	Fair
1-Cyano-4-phenyl-1,3-butadiene	Norm	..	Poor	Fair
1-Cyano-1,4-diphenyl-1,3-butadiene	Ret	Waxy- brittle	..	..
Vinyl benzoate[f]	Inh	..	..	..
Ethyleneglycol dicinnamate	Acc[e]	Nonco- herent	..	..
Methyl-4-nitrocinnamate	Ret	Nonco- herent	..	..
Methyl α-cyano-β-phenyl acrylate	Acc[e]	..	Poor	Poor
1-Phenyl-4-cyano-4-carboethoxy-1,3- butadiene	Acc[e]	Good	Fair	Good
Methyl-o-cyanocinnamate				
59° isomer	Norm	Good	Poor	Fair
92° isomer	Acc[e]	Good	Good	Good
Isocyclic amines				
Aminostyrene[f]	Inh	Powder	..	..
Crotonanilide	Inh	Cheesy	..	..
Methacryl anilide	Acc[e]	Flaky	Good	VG
Methacryl p-nitroanilide	Inh	..	..	..
Methacryl-m-toluidide	Ret[e]	Hard	Good	VG
o-Cyanocinnamic anilide, *trans?* (m.p. 186–187° C)	Norm[e]	Fair	Poor	Poor
o-Cyanocinnamic anilide, *cis?* (m.p. 130–135° C)	Ret[e]	Fair	Poor	Poor

TABLE V—*Continued*

ELASTOMERS FROM BUTADIENE WITH VINYL COMPOUNDS

Second monomer	Polymeri-zation rate[a]	Mill appearance[b]	Tensile strength[c]	Elonga-tion
Isocyclic amines—*Continued*				
o-Cyanocinnamic anilide m-nitro-anilide	Inh	. .	. .	. .
Methacryl p-hydroxyanilide	Inh	. .	. .	. .
Methacryl p-aniside	Inh	. .	. .	. .
Heterocyclic compounds				
2-Vinylpyridine	Acc	Good	VG	VG
5-Ethyl-2-vinylpyridine	Acc	Good	VG	VG
β(α-Furyl)acrylic acid	Inh	. .	. .	. .
Furylacrylic acid	Inh	. .	. .	. .
Methyl-β-furylacrylate	Acc[e]	Good	Good	Good
Allyl-β-furylacrylate	Acc[e]	Dry	Poor	Poor
Furfuryl methacrylate	Acc[e]	Good	. .	. .
β-Furyl acrylonitrile[f]	Inh	. .	. .	. .
Ethyl α-cyano-β-furylacrylate	Inh	. .	. .	. .
Furoic anilide	Norm[e]	Poor	. .	. .
β-Nitrofurylethylene	Inh	. .	. .	. .
1-Furyl-1-buten-3-one	Acc[e]	Good	Good	Good
1-Furyl-5-methyl-1,4-hexadien-3-one	Inh	. .	. .	. .
1-Furyl-3-phenyl-1-propen-3-one	Acc[e]	Good	Good	Good
Chlorovinylethylene oxide	Inh	. .	. .	. .
Ethylene sulfide	Inh	Powder	. .	. .
Propylene sulfide	Inh	Plastic	. .	. .
Indole	Inh	. .	. .	. .
2-Methylindole	Inh	. .	. .	. .
N-Methyl maleicimide	Inh	. .	. .	. .
N-Butyl maleicimide[f]	Ret	Soft	. .	. .
N-Cyclohexyl maleicimide	Ret[e]	Good	Fair	VG
N-Methyl citroconicimide	Ret[e]	Good	. .	. .
N-Allyl maleicamide	Inh	Powder	. .	. .
N-Vinyl succinimide	Inh	. .	. .	. .
Terpene peroxide	Inh	. .	. .	. .

[a] Acc = accelerated; Norm = normal; Ret = retarded; Inh = inhibited.
[b] Good means the band on the mill was smooth and unbroken; Fair, the band was somewhat broken and rough; Poor, the band was difficult to maintain. Certain of the poor-milling polymers are described more specifically.
[c] Poor, less than 1,500 lbs. per sq. in.; Fair, 1,500–2,000 lbs.; Good, 2,000–3,000 lbs.; Very good, above 2,000 lbs.
[d] Poor, less than 250%; Fair, 250–350%; Good, 350–450%; Very good, above 450%.
[e] Product contains appreciable amounts of second monomer.
[f] Polymerized in acid emulsions.

These results indicate that minor changes in the structure of the second monomer can have a pronounced effect on its ability to form an interpolymer with butadiene, possibly as a result of differences in the firmness of the electron bondage. For example, high yields of elastomer were obtained from mixtures of butadiene and 2-nitro-2-methylpropyl methacrylate; mixtures of butadiene and 2-nitrobutyl methacrylate failed to yield significant amounts of elastomer in either acid or alkaline systems. A similar influence of structure on ease of formation of polymers is found in the case of crotonic anilide and methacrylic anilide. Mixtures of crotonic anilide (CH_3—CH=$CHCONHC_6H_5$) and butadiene gave only small amounts of cheesy product in either acid or alkaline emulsions; butadiene and methacrylic anilide [CH_2=$C(CH_3)CONHC_6H_5$] gave high yields of elastomer.

STRUCTURE OF POLYMERS

The polymerization of mixtures of different polymerizable materials may result in the formation of elastomers consisting of long chains, each of which contains a variable number of units of each of the monomeric materials; or it may result in the formation of a mixture of polymers, each made up of units of only one of the polymerizable compounds. A given elastomer may contain mixtures of both types of polymers. In this laboratory it has been the custom to refer to the first class of elastomers as interpolymers and to the second as copolymers, although the term copolymers is used commonly to cover both classes.

It is often difficult to determine precisely which type of polymer is present. In some cases it is possible to determine the presence of a particular type by visual examination, physical separation, and analysis. In other cases simple extraction with solvents and analysis may serve to show the presence of different types of products. Comparison of the physical properties of the products formed by polymerization of mixtures with those formed by mill blends offers some indication of the presence of true interpolymers. Freeze resistance is believed to be a significant means of determining the difference between true interpolymers and mixtures. In certain cases determination of the index of refraction gives valuable information.

The presence of an element, such as nitrogen or chlorine, which can readily be determined quantitatively is frequently helpful in studying copolymers. For example, a butadiene-acrylonitrile copolymer was dissoved in benzene (5 per cent cement) and, at 40° C, diluted with 58 grams ethyl alcohol per 100 grams cement. The mixture was cooled to 28° C and, on standing, separated into two layers. The solvents were removed by evaporation, the product of higher molecular weight was redissolved, and the treatment repeated. The original elastomer was separated into four fractions of different solubilities. The data obtained with these fractions indicate there is comparatively little difference in the chemical composition of the various fractions, i.e., the product is essentially a true interpolymer. The least soluble fraction does contain slightly less nitrogen than the most soluble fraction. The viscosities of cements made from these fractions, as determined in a Gardner-Holdt bubble tube, indicate a wide difference in molecular weight:

Relative solubility	Percentage of original	Nitrogen content (%)	Bubble-tube viscosity of 9.5% benzene cements (sec.)
	100	7.31	9
1	23	7.30	2
2	23	7.24	3.7
3	18	7.34	12
4	36	6.99	300

Results obtained by polymerizing, in both acid and alkaline systems, a number of different mixtures of butadiene and acrylonitrile indicate that the composition of the copolymer is chiefly dependent on the composition of the monomer mixture, even if the polymerization rates vary widely. These data (Figure 12) indicate a linear relation between the compositions of the monomer mixture and the resulting copolymer. According to these results, a monomer mixture containing a little over 35 per cent acrylonitrile should give a quantitative yield of elastomer of the same composition as indicated by the insection of the dotted line for a uniform copolymerization and the experimentally de-

termined relation. Copolymers made from higher butadiene-acrylonitrile ratios contain a higher acrylonitrile content than the monomer mixtures; those made from low butadiene-acrylonitrile ratios contain a lesser portion of the nitrile. While this generalization holds for this particular combination of monomers, it is not necessarily applicable to all other combinations. In fact, with some mixtures one monomer may polymerize to yield a product containing little or none of the second material.
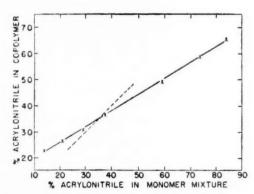
Fig. 12.—Relation between composition of monomer mixture and copolymer for butadiene-acrylonitrile.

PROPERTIES OF CERTAIN COPOLYMERS

The proportion of the second monomer in the starting mixture markedly affects both the rate of polymerization and the properties of the resulting polymer. Improvements in certain properties obtained by a selected ratio of monomers may be accompanied by deficiencies in other properties. For example, a higher retention of tensile strength at elevated temperatures may coexist with poorer freeze resistance (Table VIII). Certain of the second monomers listed in Table V, such as methyl and butyl methacrylate[26], methylvinyl ketone[27], dimethylvinylethynylcarbinol[28], in combination with butadiene and isoprene, have been studied in more detail, and some of the results are described in the following sections. The copolymers were compounded according to the basic formula: copolymer 100, phenyl-β-naphthylamine 2, stearic acid 2, zinc oxide 5, MPC black 50, sulfur 2, mercaptobenzothiazole 1.

Methacrylate Copolymers.—When mixtures of butadiene and methyl methacrylate were polymerized in an ammonium oleate emulsion containing 0.8 part excess ammonia and 1 part ammonium persulfate, the polymer yield obtained in 40 hours at 30° C was found to increase considerably with increase in methyl methacrylate–butadiene ratio (Figure 13). The variation in properties with monomer ratio is shown by the data of Table VI.

In a practical road test, a tire made from a 70 butadiene–30 methyl methacrylate elastomer was only slightly inferior to a high grade rubber control. These polymers made with methyl methacrylate compare favorably with those made with styrene in vulcanizate properties, and are actually superior in processability and oil resistance.

Data obtained in determining properties, such as freeze resistance, kerosene absorption, Schopper rebound and Shore durometer hardness, of vulcanizates
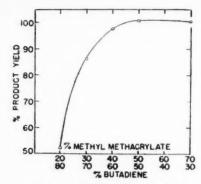
Fig. 13.—Effect of monomer ratio on yield of elastomer for butadiene-methyl methacrylate in ammonium oleate emulsion.

TABLE VI

PROPERTIES OF BUTADIENE–METHYL METHACRYLATE ELASTOMERS

(Cure, 30 minutes at 153° C)

% Methyl methacrylate	Stress at 300% (lbs. per sq. in.)	Tensile strength (lbs. per sq. in.)	Elongation at break (%)	Kerosene absorption[a] (vol.-%)
20	1625	3100	420	209
30	1975	3400	400	217
40	2100	4350	440	110
50	. .	2525	290	105
70	. .	1400	210	48

[a] Increase in volume in 48 hours at 100° C.

of elastomers formed from mixtures of butadiene or isoprene with methyl methacrylate or butyl methacrylate are plotted in Figures 14 to 18. Butyl
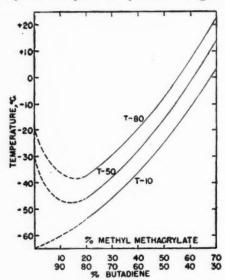
Fig. 14.—Freeze resistance of butadiene-methyl methacrylate elastomers as determined by T-50 method.
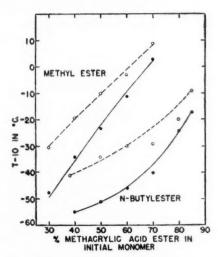
Fig. 15.—Effect of methacrylic acid esters mixed with butadiene and isoprene on freeze resistance (T-10 value) of vulcanized copolymers.
——— Butadiene copolymer.
- - - Isoprene copolymer.
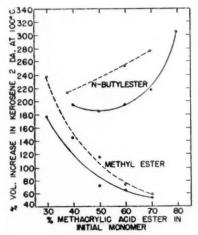
Fig. 16.—Effect of methacrylic acid esters mixed with butadiene and isoprene on kerosene absorption of vulcanized copolymers (cured 30 minutes at 153° C).
——— Butadiene copolymer.
- - - Isoprene copolymer.
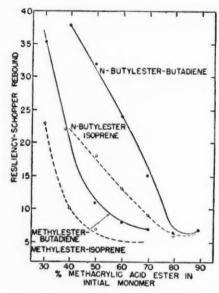
Fig. 17.—Effect of methacrylic acid esters mixed with butadiene and isoprene on resilience of vulcanized copolymers (cure 30 minutes at 153° C).
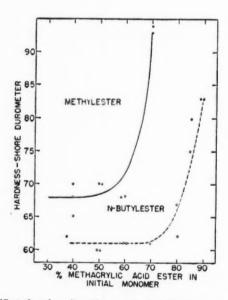
Fig. 18.—Effect of methacrylic acid esters mixed with butadiene on hardness of vulcanized copolymers (cured 30 minutes at 153° C).

methacrylate is superior to methyl methacrylate in imparting freeze resistance and resiliency, but methyl methacrylate tends to give harder, more oil-resistant vulcanizates. The T-10 results indicate that the tendency of the polymer to become brittle at very low temperatures increases with increasing methyl methacrylate content. The T-50 and T-80 results indicate that the presence of small amounts of methyl methacrylate actually improved the retention of "snap" at intermediate temperatures. Butadiene is superior to isoprene in imparting freeze resistance, oil resistance, and resiliency.

Methylvinyl Ketone Copolymers.—Mixtures of butadiene and methylvinyl ketone can be polymerized to give good yields of copolymers whose vulcanizates exhibit to an unusual degree a combination of kerosene and freeze resistance (Table VII). In fact, for a given freeze resistance they are superior to buta-

TABLE VII

PROPERTIES OF BUTADIENE-METHYLVINYL KETONE ELASTOMERS

Methyl-vinyl ketone (%)	Yield (%)	Stress at 300% (lbs. per sq. in.)	Tensile strength (lbs. per sq. in.)	Elonga-tion (%)	Kerosene absorp-tion[a] (%)	Freeze resistance (° C)	
						T-20	T-50
20	93	. .	1210	120	94	−63	−54
30	80	1020	2720	520	76	−50	−40
40	91	1640	3080	420	35	−42	−37
50	91	2890	3050	310	23	−36	−30
60	82	1780	3450	470	14	−28	−20
80	32	1210	2890	520	5	−20	−10

[a] 48 hours at 100° C.

diene-acrylonitrile polymers in kerosene resistance. These particular elastomers were made by polymerizing at 30° C in a myristylamine $[CH_3(CH_2)_{12}\text{-}CH_2NH_2]$-hydrochloric acid system catalyzed with ammonium persulfate and containing no modifier; good elastomers have also been made in oleate, or preferably Loral sulfate, systems. Methylvinyl ketone is a strong lachrymator, and it is difficult to obtain a vulcanizate of its diene copolymers free from the characteristic odor.

Dimethylvinylethynylcarbinol Interpolymers.—$(CH_3)_2COH\text{—}C\equiv C\text{—}CH=CH_2$ gives excellent elastomers when interpolymerized with butadiene. Typical data (Table VIII) were obtained with a system containing 4 parts oleic acid, 1 part Daxad 11, 0.5 part sodium hydroxide in excess of that required to neutralize the oleic acid, 1 part potassium persulfate, 0.05 part potassium ferri-cyanide, and 1 part DD thiol. The data show that good copolymers are obtained with 15 to 30 parts of the carbinol. It is believed to be significant that the heat build-up reaches a minimum when 20–30 parts of carbinol are used. The 70 butadiene–30 carbinol copolymer is especially interesting; at approximately the same state of cure (judged by modulus) as the 10 and 15 per cent carbinol copolymers, the tear resistance, heat build-up, and tensile strength at 70° C reach an optimum.

The possibility of using three or more monomers in forming an elastomer is intriguing and susceptible of an infinite number of variations. The replacement of part of the styrene in the GR-S formula with dimethylvinylethynylcarbinol was investigated in some detail, and mixtures of 75 butadiene–20 styrene–5 dimethylvinylethynylcarbinol gave[29] elastomers superior to GR-S in millability, tensile properties, and low heat build-up under flexing, but not superior to those made from butadiene with 20 or 30 parts of the carbinol and no styrene.

TABLE VIII

PROPERTIES OF BUTADIENE–DIMETHYLVINYLETHENYLCARBINOL ELASTOMERS
COMPOUNDING FORMULA (CURED 30 MIN. AT 141° C)

COMPOUNDING FORMULA (CURED 30 MIN. AT 141° C)

Elastomers	100
Phenyl-β-naphthylamine	2
Zinc oxide	5
MPC black	50
Stearic acid	2
Sulfur	1.5
Heliozone	1.5
Process oil	3
Benzothiazyl-2-monocyclohexylsulfonamide	1.3

Dimethylvinylethynylcarbinol (parts)	10	15	20	30	50
Tested at 25° C					
Stress at 300% (lbs. per sq. in.)	1050	900	1525	1100	1390
Tensile strength (lbs. per sq. in.)	2275	2875	3000	4400	3220
Elongation at break (%)	465	580	460	655	480
Tear resistance (lbs.)	175	145	165	290	..
Shore durometer hardness	59	57	59	58	..
Heat build-up in 20 min. on Goodrich					
flexometer (¼-in. stroke)	52	53	44	44	..
Resiliency (Yerzley)	53	49	56	54	..
Tested at 70° C					
Tensile strength (lbs. per sq. in.)	1025	1400	1850	2450	..
Tear resistance (lbs)	140	180	135	285	..
Kerosene absorption (% volume in-					
crease in 48 hrs. at 100° C)	180	155	130	103	..
Freeze resistance (° C)					
T-10	−62	−57	−46	−29	−16
T-50	−43	−42	−36	−22	−7
T-80	−32	−31	−28	−14	−1

CONCLUSION

In any study of polymerization, careful consideration must be given to factors such as type and concentration of emulsifying agent, concentration of monomer, temperature, catalyst, and certain added chemicals which may have a marked effect on the results obtained.

It is possible to make elastomers of considerable utility from mixtures of butadiene and many other polymerizable compounds. Several of these are superior to those made from butadiene and styrene in particular respects; but considering availability and cost of raw materials, this work has not uncovered any butadiene copolymers which would have been preferred over those made with styrene or acrylonitrile in the period of national emergency. The possibility of obtaining high grade elastomers from the diene hydrocarbons alone appears to justify further investigation.

ACKNOWLEDGMENT

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ABSORPTION OF OXYGEN BY RUBBERS *

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Several workers have investigated the reaction between rubber and oxygen, in the important initial stages over which the rubber retains its rubbery qualities, by following the rate of disappearance of gaseous oxygen in a closed system. Particular attention has been directed toward establishing the effect of oxygen pressure on the rate of the reaction. This is fundamentally important. Also, in the surface of the rubber the oxygen concentration consistent with the pressure of oxygen in the gas phase is maintained by dissolution, whereas in the interior, oxygen can be supplied only by the diffusion of already-dissolved oxygen. At any point in the interior the concentration which can be built up is determined by the rate at which oxygen diffuses in from higher concentration regions and out to lower concentration regions and by the rate at which it is used up by combination. In the interior, therefore, the oxygen concentration, and hence the reaction rate, corresponds to a gas pressure different from that of the surrounding free gaseous oxygen.

One method which was used, notably by Williams and Neal[1] and Morgan and Naunton[2], for the fundamental investigation of the rubber-oxygen reaction has the advantages of simplicity and ease of operation. It consists in confining the rubber specimen in an oxygen-filled vessel connected to a vertical tube dipping into mercury. Oxygen pressure falls spontaneously as oxygen combines, and mercury ascends the vertical tube. At any particular stage in the experiment the position of the mercury meniscus in the tube gives the oxygen pressure, and its rate of movement gives the rate of combination of oxygen with the rubber. Williams and Neal, using finely subdivided acetone-extracted rubber specimens, conclude from their experiments that rate of oxygen combination is independent of oxygen pressure over most of the absorption. Morgan and Naunton, using similar specimens and continuing the work of Williams and Neal, chiefly with regard to the effect of temperature, put forward a chain reaction theory for the mechanism of the reaction, on the basis of the same conclusion.

The work of the investigators mentioned, however, is at variance with that of others using different experimental techniques[3] and, furthermore, their experimental method is not free from criticism. For example, Kohman[4], working at constant oxygen pressure over the whole range of oxidation up to resinification, showed that the reaction is autocatalytic; consequently time effects other than those arising from the diffusion process may be operative and may vitiate the results of manometric experiments. Also, investigators in this field are generally agreed that the higher oxygen pressures favor more rapid oxidation (usually judged by the decay of tensile properties), as shown by the common practice of assessing the oxidation resistance of technical products by accelerated aging in the Bierer-Davis pressure bomb. Furthermore, although a

quantity of oxygen sufficient to cause a considerable modification of the physical properties of the rubber combines during an experiment[5] direct comparisons are made between the initial and final stages without evidence that the changed degree of oxidation has no effect on oxidation rate.

The investigation outlined in the present account was commenced with the following aims in view: (1) to try out a modified manometric apparatus which was believed would have advantages over the simple Williams and Neal type; (2) using this apparatus to investigate the value of the manometric method as a tool for a fundamental investigation[6] and as a means of determining and comparing the resistance to oxidation of specimens of technical rubbers; (3) to investigate the physical chemistry of the reaction between rubber and oxygen. A preliminary note on some of the results of this investigation has been published previously[7].

MODIFIED MANOMETRIC APPARATUS

The apparatus differed considerably in detail from the simple Williams and Neal apparatus, but was identical in principle. It was so designed that absorptions could be followed over pressure changes of about 15 cm. of mercury, starting from any desired initial pressure less than about 3 atmospheres. It was independent of the pressure of the atmosphere and its fluctuations. The apparatus was described previously[8] in connection with experiments to determine the solubilities and diffusion coefficients of gases in rubbers. By the use of this apparatus the rate of oxygen absorption at any pressure within the chosen range may be calculated from readily ascertainable data.

EXPERIMENTS WITH MANOMETRIC APPARATUS

The state of subdivision necessary for substantially uniform oxygen concentration and, hence, oxidation throughout a rubber specimen depends on the susceptibility of the latter to oxidation, the more readily oxidizable rubber requiring the finer subdivision. It was considered possible that, with quite large specimens of more slowly oxidizing rubbers, oxidation might be substantially uniform and absorption rates little affected by diffusion. An experiment was carried out with this possibility in mind. The specimens were made from the following mixture, in parts by weight:

Rubber (smoked sheet)	100
Sulfur	3
Zinc oxide	3.5
Stearic acid	1.5
Mercaptobenzothiazole	1
Agerite White	0.25

The mixture was vulcanized by heating for 30 minutes at 148° C in closed molds. The specimens were in the form of cylindrical rods, about 5-mm. in diameter and 15 cm. long (specimens A and B), square sectioned rods about 1 × 1 mm. in cross-section and not less than 5 cm. long (specimen C), and cubes of about 1.5-mm. side (specimen D). The surface areas of the specimens were, approximately, 25 sq. cm. (A and B), 75 sq. cm. (C), and 120 sq. cm. (D).

The experiment was carried out in darkness at 45° C, starting at a pressure of about 80 cm. of mercury. The period allowed for solution equilibrium was 24 hours. (A calculation based on the known solubility and diffusion coefficient of oxygen in the rubber showed that, if no chemical combination had occurred between the oxygen and the rubber, the rate of solution in the cylin-

drical specimens, at a pressure of 1 atmosphere, would have been about 4.2 $\times 10^{-8}$ gram oxygen per gram rubber per day after 12 hours, and about 0.9×10^{-12} gram oxygen per gram rubber per day after 24 hours.)   In each case the mercury ascended the capillary at a constant rate over the 15-cm. range.   The absorption rates, calculated for the conditions when the pressure of oxygen in contact with the specimen was 1 atmosphere, were as follows:

Specimen	A	B	C	D
Absorption rate (g. oxygen per g. rubber per day) $\times 10^{-5}$	4.92	5.37	5.67	4.51

The experiment was repeated using fresh specimens, one of the cylindrical specimens being given an 18-hour aging pretreatment in the Geer oven.   Again in all cases the mercury ascended the capillaries at a constant rate.   The absorption rates, calculated as before for an oxygen pressure of 1 atmosphere, were as follows:

Specimen	A	B	C	D
Absorption rate (g. oxygen per g. rubber per day) $\times 10^{-5}$	5.40	5.27	9.54	6.06

The specimen subjected to Geer oven aging was B.

Although the agreement between the results of these experiments is poor, the results show that there was no consistent effect of subdivision.   Thus with this slowly oxidizing rubber it appears that oxidation under these conditions is substantially uniform throughout all of the specimens.   Several other investigators[9] showed that, with slowly oxidizing rubbers, it is not necessary to go to an extreme state of subdivision—for example, crumb—to eliminate diffusion as a rate-determining process.   Calculations confirm that diffusion effects had negligible influence on the results.

In the apparatus of Williams and Neal the change in internal free volume of the specimen tube during the spontaneous pressure change was negligible. Their conclusion that the rate of oxygen combination is independent of pressure depended on this experimental arrangement.   The design of the present modified apparatus was such that the internal free volume change was an appreciable fraction of the total.   In these experiments, therefore, the rate of oxygen combination was lower, the lower the oxygen pressure.

An experiment was carried out to determine the effect of oxygen pressure on the absorption rate over a wide pressure range, using five identical cylindrical specimens of 5-mm. diameter.   The specimens were made from the mixture described and were kept for 3 days under vacuum in darkness before test. In this experiment the pressure of the oxygen in contact with the specimens was reduced alternately in one of two ways: (1) It was allowed to fall spontaneously over a small pressure range as absorption proceeded or (2) it was artificially reduced at intervals by withdrawing oxygen from the apparatus. In this way, starting from a pressure of about 180 cm. of mercury, absorption rates were followed over spontaneous pressure decrease steps of about 10 cm. down to about 12 cm. of mercury.   When the pressure was changed by withdrawing oxygen, 24 hours were allowed for solution equilibrium.   The experiment was carried out in darkness at 45° C.   The results are given in Table I.   The specimens were kept for 3 days under vacuum in darkness, and a repeat experiment was carried out on them.   The results were in general agreement with those of the first experiment.

Starting with pressures of 180, 140, and 84 cm. of mercury, the rate of rise of mercury in the capillaries during the spontaneous pressure-fall steps was constant in any one case, but was not the same for any one specimen for the

TABLE I

EFFECT OF OXYGEN PRESSURE ON OXYGEN ABSORPTION RATE OF CYLINDRICAL SPECIMENS OF A SLOWLY OXIDIZING RUBBER AS DETERMINED WITH MODIFIED MANOMETRIC APPARATUS

Oxygen pressure (cm. Hg)	Absorption rate (g. oxygen per g. rubber per day) $\times 10^{-5}$				
	a	b	c	d	e
180.2	11.64	11.93	11.66	10.81	13.20
171.2	11.34	11.62	11.35	10.43	12.80
140.2	10.00	9.82	10.04	9.07	12.10
130.2	9.71	9.47	9.74	8.73	11.69
84.2	7.82	8.44	8.80	7.70	9.97
79.2	7.77	8.27	8.66	7.52	9.77
44.2	5.77	6.05	5.84	5.77	8.03
37.2	5.61	5.88	5.68	5.57	7.79
20.2	3.79	3.55	3.90	3.69	4.98
12.2	2.26	2.36	2.54	2.11	2.79

three steps. With a starting pressure of 44 cm. of mercury, there was a tendency in all cases for the rate to decrease with spontaneous decrease in oxygen pressure. At a starting pressure of 20 cm. of mercury the tendency was marked. In Table I absorption rates have been calculated for the oxygen pressures at the beginning and at the end of the spontaneous pressure changes.

It is seen that the absorption rate is markedly dependent on oxygen pressure. This is in agreement with the findings of Ingmanson and Kemp[10]; by following decay of physical properties, they showed that, for oxygen pressures less than about 4 atmospheres, absorption rate increases with oxygen pressure. The results, however, are unsatisfactory, because a graph shows that, in any one case, the short curves corresponding to the spontaneous pressure decreases do not lie on one continuous curve. Very roughly, absorption rate is proportional to the square root of the oxygen pressure, a result in agreement with the findings of van Amerongen[6] and of Milligan and Shaw[11]. These experiments show that results with the manometric apparatus are not independent of the arbitrary conditions of the experiment. The progressive change in the condition of the rubber at each step, due to oxidation during the preceding steps, does not affect the absorption rate at that particular step, because the repeat experiment on the same specimens gave similar results. The reproducibility of results with the same specimen, however, does not exclude the possibility that the initial stages of oxidation in a particular step might affect the later stages of that step.

In all the experiments with this modified manometric apparatus the agreement was poor among results of experiments differing only in insignificant detail. This was considered surprising in view of the known reliability of the apparatus used in a slightly different connection[8], and in view of the fact that the result of each individual determination could be quoted with considerable accuracy—that is, having regard only to the accuracy with which the relevant experimental data could be ascertained.

From the nature of the results of these experiments it appears that they are affected by an unappreciated factor inherent in the method. Moreover, it is fundamentally unsound to allow both of the interdependent variables, oxygen pressure and oxygen combination rate, to change without control. All further work was carried out at constant oxygen pressure.

These criticisms of the manometric method do not necessarily apply to the work of Dufraisse[12], who used it under carefully standardized conditions as a routine test for the estimation of the oxidizability of various rubbers.

CONSTANT PRESSURE APPARATUS

Milligan and Shaw[11] and van Amerongen[6] described apparatus for measuring the oxygen absorption of rubbers at more or less constant total gas pressure by methods involving the manual adjustment of the pressure from time to time. These methods were unsatisfactory for the present purpose. Kohman[4] described apparatus in which the pressure was automatically kept constant. It was, however, designed to measure the total absorption of oxygen over the complete range up to resinification, and was not considered capable of sufficient refinement to allow accurate measurement of very small oxygen absorption rates.

Figure 1 shows the apparatus designed and used for measuring oxygen absorption rates at constant pressure. It consisted of bulb B, of about 700-cc. capacity, with an extension, D, of 2-cm. diameter and 6-cm. length connected to a horizontal capillary, C, 14 cm. long and uniform in bore (0.0104 cc. per cm.), marked off in centimeters by etched lines. The end of the capillary farthest
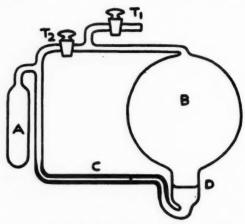
Fig. 1.—Apparatus for determining oxygen rates of rubbers at constant oxygen pressure.

from bulb extension D was connected directly to specimen bulb A (which was sealed on afresh for each new specimen) and continued through tap T_2 to the top of bulb B. The system contained a side tube with a tap, T_1. Bulb extension D served as a reservoir for a light paraffin oil freed from readily volatile constituents. The quantity of oil used was such that, when the capillary was horizontal, it rose into the capillary, and the equilibrium position of its meniscus was at the end near the reservoir. Because of the great cross-sectional area of the reservoir compared with that of the capillary, movement of the oil meniscus along the capillary caused only a very small change in oil level in the reservoir. The oil meniscus in the capillary showed little tendency to move toward the reservoir when it was placed at the end of the capillary farthest from the reservoir and was free to move. Adjustment of the oil meniscus to any desired position in the capillary could be accomplished by tilting the apparatus with tap T_2 open.

For normal use the apparatus was connected by means of the side tube and tap T_1 to a mercury manometer, a vacuum pump, and an oxygen cylinder. During an experiment the whole of the apparatus shown in the diagram was con-

tained in a thermostat of temperature constant to within 0.02°C.   The oxygen absorption rate of a rubber specimen was deduced from the movement of the oil meniscus in the capillary when, with the apparatus filled with oxygen at the desired pressure, gaseous connection between the specimen bulb and the large bulb was severed by turning off tap T_2.   The disappearance of oxygen from the gaseous phase in the specimen bulb caused the oxygen in the large bulb to force the oil along the capillary.   The volume swept out by the oil meniscus was a measure of the volume of oxygen absorbed.

Calculation shows that using the following equation as an approximation:

$$v = bx \left[\frac{V_1 + V_2}{V_1} \right]$$

where V_1 = internal free volume on large bulb side of apparatus from oil sur-
face in reservoir to tap T_2

V_2 = internal free volume of specimen bulb and connections from oil meniscus in capillary to tap T_2

b = cross-sectional area of capillary

v = volume of oxygen (measured at pressure of experiment) absorbed by specimen

x = movement of oil meniscus along capillary resulting from ab-
sorption

The error involved for an average actual value of V_2 = 30 cc. is about 0.7 per cent at 1 atmosphere, 1.3 per cent at $\frac{2}{3}$ atmosphere, and 2.5 per cent at $\frac{1}{3}$ atmosphere.   This approximation was considered to be sufficiently close; the factor $(V_1 + V_2)/V_1$ was applied in the calculation of results.   The change of pressure of the oxygen surrounding the specimen, as the oil meniscus moves 10 cm. along the capillary, is about 0.02 per cent of the original pressure.   This was considered to be negligible.

The use of oil instead of mercury as the indicating liquid in the apparatus needs justification.   Its main advantages and the reasons for which it was chosen are twofold: (1) the oil shows no tendency to stick in capillaries; (2) gas pressure errors arising from incorrect leveling of the capillary and from the change in liquid level in the reservoir due to movement of the meniscus in the capillary are minimized because of the low specific gravity of the oil.   The dis-
advantages are its volatility at low pressures and its solvent power for gases. The former was overcome by never using pressures lower than 0.2 cm. of mer-
cury.   When the complete removal of oxygen from the apparatus was neces-
sary, it was displaced by nitrogen.

The apparatus was tested in several ways to ensure that the rate of move-
ment of the oil meniscus in the capillary was an accurate measure of the rate of disappearance of gas through the specimen tube side arm.   All of the tests were satisfactory and showed that the apparatus was capable of giving trustworthy results.   The only correction necessary was that arising from the dissolution of oxygen in the oil of the reservoir; the correction was necessary only in de-
terminations with rubbers giving very slow meniscus movement rates (of the order of 10 cm. per day) during the first few hours after the pressure change. In the calculation of the results the appropriate correction, determined by experiment, was applied where necessary.   The method of using the apparatus for the determination of oxygen absorption rate of rubber was as follows:

The rubber specimen was sealed into a glass bulb with as little free space left as was conveniently possible.   This specimen bulb was then sealed onto

the apparatus, and, when required, an opaque covering was placed around it. The completed apparatus with tap T_2 open was placed in the thermostat and, together with all connecting tubes, alternately evacuated and filled with oxygen until all gases other than oxygen were removed. The apparatus was then filled with oxygen as the desired pressure. Oxygen began to dissolve in the rubber and was used up by oxidation. After a time interval determined by experiment (Table II), absorption was entirely due to chemical combination of oxy-

TABLE II

RATE OF DISSOLUTION IN 0.2 CM. CUBES OF GAS-FREE SMOKED
SHEET RUBBER AT 40° C, IN COMPLETE DARKNESS

Oxygen pressure* (cm. Hg)	Time after start (hrs.)	Rate of movement of oil meniscus (cm. per hr.)
72.9	0.15	560
	0.25	220
	0.55	28
36.7	0.15	480
	0.35	105
	0.67	8
72.4	0.15	468
	0.25	242
	0.40	86
	0.50	42
	0.60	14
74.3	0.05	1590
	0.10	860
	0.15	550
	0.25	253
	0.37	105
	0.48	48
	0.80	4

* Rates of movement at different pressures are strictly comparable because solubility, measured as volume of gas at pressure of the experiment, is independent of gas pressure.

gen. Tap T_2 was turned off, and the rate of disappearance of oxygen from the gas phase in the specimen bulb was measured by the rate at which the oil moved along the horizontal capillary. When the oil reached the specimen tube end of the capillary, tap T_2 was opened and the meniscus returned to the reservoir end ready for a subsequent determination. Similar determinations at other pressures could be made either by the evacuation procedure or by simply introducing or withdrawing oxygen.

The work carried out with the constant pressure apparatus and recorded here is in the nature of a preliminary investigation searching out the field for future, more rigid, treatment. Nevertheless, a broad interpretation confirms the essential invalidity of deductions based on work carried out with the manometric type of apparatus, indicates the reasons, gives the required background for a general investigation of the oxygen-rubber reaction, and gives a new basis for the theoretical treatment of the problem.

RAPIDLY OXIDIZING VULCANIZED RUBBER

To check the reproducibility of results on a rubber specimen, an experiment was carried out with a rapidly oxidizing rubber prepared by heating the following mixture for 40 minutes at 145° C in a closed mold (in parts by weight):

Rubber (deproteinized by centrifugal purification of latex,   100
  and containing 0.25% added antioxidant)
Sulfur   3
Zinc oxide   5
Diphenylguanidine   1.5

The 8-mm.-thick slabs of the vulcanized material were kept at laboratory temperature in the dark and, when required for testing, were reduced to a crumb of particle diameter about 0.3 mm. by passage through a cold friction mill at a tight nip. The temperature of the experiment was 40° C, the oxygen pressure 75.2 cm. mercury, and the time allowed for solution equilibrium 2 hours. Five estimations were made without altering the conditions, the rates of movement of the oil meniscus being 1.80, 1.74, 1.68, 1.66, and 1.84 cm. per minute. The total consumption of oxygen during the experiment was about 0.04 per cent by weight, 0.02 per cent during the equilibrium period, and 0.02 per cent during the absorption rate measurements. The results showed merely random variation; no consistent trend was apparent with increase in combined oxygen proportion.

Ingmanson and Kemp[13], working at more or less constant pressure and estimating combined oxygen by direct weighing and by decay of physical properties, also found that the absorption rate of antioxidanted rubbers attains a constant value. It is probable that in Kohman's work[4] the antioxidant became oxidized away in the early stages, and the behavior noted was the autocatalytic reaction of nonantioxidized rubber. Another specimen of the same rubber mixture was used to find the effect of oxygen pressure on absorption rate. The experiment was carried out at 40° C, and the time allowed for solution equilibrium after a pressure change was 30 minutes. Two experiments were carried out on the same specimen on consecutive days, with the apparatus left evacuated overnight. Figure 2 shows the results. The total consumption of oxygen during the first experiment was about 0.13 per cent by weight on the
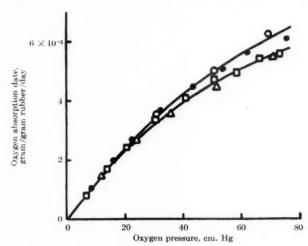
FIG. 2.—Effect of oxygen pressure on constant-pressure absorption rate of diphenylguanidine-vulcanized deproteinized rubber.

	Falling pressure	Rising pressure
First experiment	●	○
Second experiment	□	△

rubber, and during the second, about 0.16 per cent. The good agreement between the results with increasing oxygen pressure and those with decreasing pressure shows that 30 minutes was a sufficient time for equilibrium and that an increase in combined oxygen proportion of the order of 0.15 per cent is without considerable effect on oxygen absorption rate. The results show that oxygen absorption rate is greater, the greater the oxygen pressure. This is contrary to the findings of Williams and Neal and Morgan and Naunton, but is in agreement with the results of the experiment already described here, in which the oxygen pressure was artificially reduced at intervals in the mano-metric type of apparatus.

SMOKED SHEET RUBBER

A piece of smoked sheet rubber was taken from the center of a substantial block and passed through a cold friction mill at a tight nip to reduce it to a thin, rough sheet of about 0.5-mm. average thickness. Smoked sheet rubber is
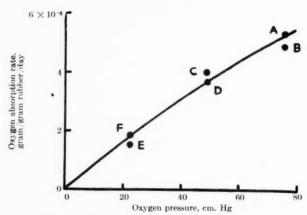

Fig. 3.—Effect of oxygen pressure on constant-pressure oxygen absorption rate of unvulcanized smoked sheet rubber.

known to absorb oxygen at a comparatively slow rate, and it was considered that the ratio of surface area to volume ratio of the specimen in this form was sufficiently great to ensure practically uniform oxygen concentration through-out the rubber during the oxidation. This was substantiated by calculations given later in the paper. A rectangular piece of the sheet was placed on a piece of filter paper, and filter paper and specimen were rolled together loosely on a glass rod for sealing into the specimen bulb. Absorption rate determina-tions were carried out on this specimen at several oxygen pressures. The equilibrium period—that is, the period during which the pressure was unaltered, immediately before an absorption rate determination—was in no case less than 40 hours and in most cases was considerably more. The temperature of the experiment was 40° C. The results are shown in Figure 3. Determinations A, D, E, and F were, for the most part, carried out overnight—that is, in darkness—whereas B and C were carried out under conditions of feeble illumi-nation by stray light. The total consumption of oxygen was about 0.005 per cent by weight on the rubber. At the conclusion of the experiment the

specimen was found to be unchanged, as far as could be determined from its behavior on the mill.

GR-S

Absorption rate determinations carried out on a butadiene-styrene copolymer synthetic rubber composition (GR-S) gave the results shown in Figure 4. This material is not a pure substance but contains, in addition to the polymeric material, small proportions of fat acids, soaps, and antioxidants. It contains about 93 per cent by weight of the copolymer. The specimen used consisted of 0.2-cm. cubes of the untreated, unvulcanized GR-S cut from a piece taken from the interior of a substantial block. It was known that GR-S absorbs oxygen at approximately the same slow rate as does smoked sheet rubber, and it was considered that this state of subdivision was sufficient to ensure substantially uniform oxygen concentration throughout the material during oxidation. Calculations show that this was justified. The temperature of the
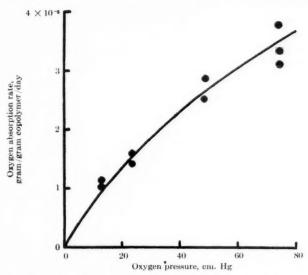
FIG. 4.—Effect of oxygen pressure on constant-pressure oxygen absorption rate of unvulcanized GR-S.

experiment was 40° C and the equilibrium period for each determination not less than 39 hours and, in most cases, considerably more. All of the determinations were carried out for the most part in complete darkness. The total consumption of oxygen was about 0.006 per cent by weight on the copolymer.

The specimen was examined at the end of the experiment and found to be insoluble in the usual solvents for fresh, unvulcanized GR-S. It had been in the thermostat at 40° C for 26 days.

In these experiments with GR-S it was found that the small amount of stray, diffuse, filtered light reaching the specimen might have a measurable effect on the absorption rate. None of the results of the experiments described, however, were considerably affected by light conditions. All of the further experiments to be described were carried out under conditions of complete darkness by enclosing the specimen tube and all adjacent glass connecting tubing in an opaque covering.

ABSORPTION RATES AFTER PRESSURE CHANGE

In the constant pressure experiments described, the oil meniscus moved along the horizontal capillary at a constant rate, and repeat determinations on the same specimen—that is, at different combined oxygen contents—gave the same results within a reasonable experimental error. There was no evidence that the absorption rate at any one pressure increased with increase in combined oxygen content. The absorption rate measurements in all cases, however, were made after an equilibrium period. This was 30 minutes in the case of the rapidly oxidizing, diphenylguanidine-vulcanized, deproteinized rubber, not less than 40 hours in the case of the smoked sheet rubber, and not less than 39 hours in the case of GR-S. These periods were allowed primarily for the attainment of solution equilibrium. An experiment was carried out, again using unvulcanized smoked sheet rubber as the specimen, first, to confirm that the dynamic equilibrium absorption rates remained constant over extended periods and, second, to investigate the absorption rate in the period immediately after the attainment of solution equilibrium in the rubber.

The specimen consisted of rough cubes of unvulcanized smoked sheet rubber, about 0.2-cm. on each side, cut from a piece taken from the center of a substantial block. Before this experiment was begun, calculation had shown that the oxidation rate of smoked sheet was sufficiently slow to enable cubes of this size to be used with negligible error from diffusion effects.

In four experiments in which oxygen was introduced into the apparatus after a long period of evacuation (to about 0.2 cm. of mercury), the rate at which oxygen dissolved was determined from time to time soon after the start. The results (Table II) show that solution is practically complete after 0.80 hour. It was considered that gas absorbed for the attainment of solution equilibrium would be a negligibly small fraction of that absorbed for combination with the rubber after 2 hours.

Two experiments were carried out in which the oxygen pressure remained constant over a long period. Determinations carried out from time to time during that period showed that absorption rates remained constant within a reasonable experimental error (Table III).

TABLE III

CONSTANCY OF ABSORPTION RATE OF SMOKED SHEET RUBBER OVER
LONG PERIODS AFTER SOLUTION EQUILIBRIUM AT 40° C IN
COMPLETE DARKNESS

Oxygen pressure (cm. Hg)	Time after start (hrs.)	Absorption rate (g. oxygen per g. rubber per day)	Total absorption (g. oxygen per g. rubber)
72.9	80–104	4.85×10^{-6}	0.36×10^{-4}
	120–132	4.83×10^{-6}	
	150–175	4.85×10^{-6}	
50.0	45– 67	3.37×10^{-6}	1.26×10^{-4}
	69– 92	3.30×10^{-6}	
	574–597	3.72×10^{-6}	
	694–723	3.57×10^{-6}	
	844–867	3.43×10^{-6}	

Experiments were performed in which the specimen was exposed to oxygen at constant pressure long enough to allow attainment of the dynamic equilibrium state of absorption at a constant rate; then the pressure was quickly reduced and again kept constant. It was found that, although the absorption rate eventually became equal to the rate consistent with the new pressure, a high initial rate persisted for several hours in diminishing degree (Table IV).

TABLE IV

INITIAL HIGH ABSORPTION RATE OF SMOKED SHEET RUBBER AFTER
PRESSURE REDUCTION AT 40° C IN COMPLETE DARKNESS

Previous exposure to oxygen		New oxygen pressure (cm. Hg)	Time after pressure change (hrs.)	Absorption rate* (g. oxygen per g. rubber per day)
Pressure (cm. Hg)	Duration (hrs.)			
74.2	143	36.5	0†	7.0×10^{-6}
			3	6.2×10^{-6}
			6	5.3×10^{-6}
			9	4.6×10^{-6}
			12	3.9×10^{-6}
			25	3.4×10^{-6}
			30	3.0×10^{-6}
			35	2.8×10^{-6}
			40	2.8×10^{-6}
			45	2.8×10^{-6}
			65	3.1×10^{-6}
73.6	144	38.6	0†	7.2×10^{-6}
			3	6.6×10^{-6}
			6	6.0×10^{-6}
			9	5.1×10^{-6}
			12	4.5×10^{-6}
			30	2.7×10^{-6}
			50	2.9×10^{-6}

* Deduced from the slope of the tangent to the scale reading against time graph.
† By extrapolation to zero time of the scale reading against time graph.

For a reduction of pressure from approximately 1 to approximately 0.5 atmosphere, the initial high rate was more than twice as great as that finally attained over 30- to 35-hour exposure to the lower pressure. The persistence of an effect on absorption rate at one pressure, immediately following previous exposure to a higher pressure, affords a possible explanation for the apparent independence of absorption rate of oxygen pressure shown in experiments carried out with the manometric type of apparatus. In this apparatus the pressure continually falls; hence the absorption rate at any stage is greater than the rate consistent with the oxygen pressure at that stage.

In the previously described experiments using unvulcanized smoked sheet rubber and GR-S, the equilibrium periods were in all cases 39 hours or more, so that the results given in Figures 3 and 4 are not vitiated by the time effects described. Although the pressure changes in the experiments using the diphenylguanidine-vulcanized, deproteinized rubber were comparatively small, the fact that equilibrium periods of 30 minutes were sufficient for the establishment of the dynamic equilibrium states suggests that the time effects already described are less marked with the more rapidly oxidizing rubber. This was confirmed in a series of experiments carried out on smoked sheet rubber vulcanized with mercaptobenzothiazole, intermediate in oxidizability between the two extremes previously investigated.

VULCANIZED SMOKED SHEET RUBBER

The unvulcanized mixture consisted of the following ingredients, in parts by weight:

Smoked sheet rubber	100
Sulfur	2.5
Zinc oxide	5
Stearic acid	1
Mercaptobenzothiazole	0.5

It was vulcanized in the form of 1-mm.-thick sheets by heating in a closed mold for 40 minutes at 1238° C. These sheets were passed through a cold friction mill at a tight nip to produce an irregular sheet of 0.2-mm. average thickness, which was rolled onto a glass rod together with a sheet of filter paper for sealing into the specimen bulb. The temperature of the experiment was 40° C. Figure 5 shows the relation between the dynamic equilibrium absorption rate and oxygen pressure; Table V gives data on the time effect resulting from a pressure change.

TABLE V

INITIAL HIGH OXYGEN ABSORPTION RATE OF VULCANIZED SMOKED SHEET RUBBER AFTER PRESSURE REDUCTION

| Previous exposure to oxygen | | New oxygen pressure (cm. Hg) | Time after pressure change (hrs.*) | Absorption rate (g. oxygen per g. rubber per day) |
Pressure (cm. Hg)	Duration (hrs.)			
75.4	50	33.3	1	4.4×10^{-5}
			24	3.6×10^{-5}
			72	3.7×10^{-5}
75.0	72	37.4	1	4.7×10^{-5}
			2	4.7×10^{-5}
			6	4.3×10^{-5}
			24	4.0×10^{-5}
			28	3.9×10^{-5}
			72	4.0×10^{-5}

* Time for solution equilibrium in the rubber, 30 minutes.
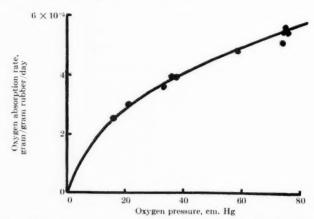
FIG. 5.—Effect of oxygen pressure on constant-pressure oxygen absorption rate of mercaptobenzothiazole-vulcanized smoked sheet rubber.

EFFECT OF EXTRACTION WITH ACETONE

A comparison was made of the oxygen absorption behavior of a rapidly oxidizing rubber, with and without previous extraction with acetone. The mixture consisted of the following ingredients, in parts by weight:

Rubber (pale crepe)	100
Sulfur	3
Zinc oxide	5
Diphenylguanidine	1.5

It was vulcanized by heating for 90 minutes at 141° C. The vulcanizate was reduced to a finely subdivided form by passage through a friction mill at a tight nip. Part of the resulting crumb was extracted for 40 hours with acetone in a Soxhlet apparatus and, after extraction, acetone was removed by prolonged evacuation. Both the extracted and the unextracted portions were kept under vacuum at room temperature in complete darkness until required for the oxygen absorption rate determinations, which were carried out at 40° C.

Specimens taken from the portion which had not undergone extraction with acetone gave results similar to those obtained for the unextracted vulcanized and unvulcanized rubbers; that is, at constant oxygen pressure, oxygen absorption rate reached a constant value which increased with increasing oxygen pressure (Figure 6).
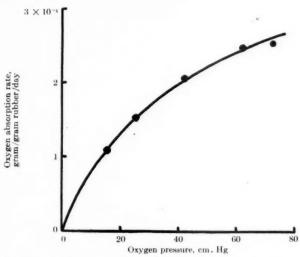
FIG. 6.—Effect of oxygen pressure on constant-pressure absorption rate of diphenylguanidine-vulcanized rubber before extraction with acetone.

In an initial stage specimens taken from the acetone-extracted portion also behaved similarly. Up to a total oxygen uptake of about $1.0–1.5 \times 10^{-4}$ grams oxygen per gram rubber, the oxidation rates reached constant values at constant pressures, the equilibrium rates being greater with the greater oxygen pressures. This stage occurred only once with each specimen.

After this proportion of oxygen had combined, however, oxidation behavior became strikingly different. At any one constant pressure the oxygen absorption rate increased as oxidation proceeded, and no dynamic equilibrium state of absorption at a constant rate was reached (Table VI). An alteration of the oxygen pressure from one constant value to a new constant value caused an approximately proportionate change in absorption rate, if due account was taken of the increase which would have occurred had the pressure remained constant during the period allowed for solution equilibrium. At the new oxygen pressure the absorption rate continued to increase from the approximately proportionate value (Figure 7). When oxidation was prevented by the removal of oxygen by evacuation or by replacement with nitrogen, subsequent exposure to oxygen gave an initial absorption rate lower than that of the previous exposure (Table VI).

TABLE VI

OXYGEN ABSORPTION OF ACETONE-EXTRACTED VULCANIZED RUBBER

Time after start (hrs.)	Oxygen pressure (cm. Hg)	Oxygen absorption rate (g. per g. rubber per day)	Time after start (hrs.)	Oxygen pressure (cm. Hg)	Oxygen absorption rate (g. per g. rubber per day)
0	Evacuation	..	19.0	Evacuation	..
15.5	76.4	..	64.0	75.7	..
16.1	76.4	1.78×10^{-3}	64.5	75.7	2.05×10^{-3}
16.4	76.4	1.88×10^{-3}	64.9	75.7	2.22×10^{-3}
16.8	76.4	1.99×10^{-3}	65.3	75.7	2.31×10^{-3}
17.2	76.4	2.08×10^{-3}	66.3	75.7	2.62×10^{-3}
17.6	76.4	2.18×10^{-3}	67.2	75.7	2.76×10^{-3}
18.3	76.4	2.35×10^{-3}	67.5	75.7	2.92×10^{-3}
18.7	76.4	2.47×10^{-3}	68.1	75.7	3.07×10^{-3}
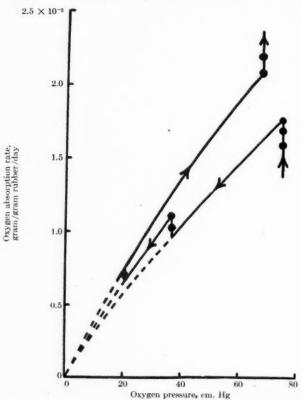
FIG. 7.—Constant-pressure oxidation behavior of diphenylguanidine-vulcanized rubber after extraction with acetone.

Extraction of natural rubber (as ordinarily produced) with acetone reduces its resistance to oxidation by removing a naturally occurring antioxidant. In the experiments recorded here, all of the rubbers examined contained either this natural antioxidant or an added antioxidant, with the single exception of the acetone-extracted specimens. It is thought that, even in the case of these specimens, a small amount of residual, natural antioxidant remained after extraction and that, during the initial oxidation stage when the behavior was

similar to that of the other specimens, the residual antioxidant was being destroyed, probably by being oxidized itself. In these experiments, therefore, only the later stage of oxidation of the acetone-extracted specimens showed the oxidation behavior of a rubber in the absence of antioxidant. In all other cases either natural or added antioxidant was present.

CONCLUSIONS FROM CONSTANT PRESSURE EXPERIMENTS

Antioxidant Present.—(1) Oxidation at constant oxygen pressure reaches a dynamic equilibrium state of reaction at a constant rate. (2) This rate is greater, the greater the oxygen pressure, but increases less rapidly than oxygen pressure. (3) If, after the attainment of the state of oxidation at a constant rate, the pressure is reduced to a new constant value, the reaction rate is initially greater than that consistent with the new pressure, but it falls gradually, over a period of several hours, to this value. This effect is more marked the less readily oxidizable the rubber.

Antioxidant Absent.—(4) The reaction rate at constant pressure increases with increase in combined oxygen proportion. (5) The reaction rate at constant pressure is reduced to a lower new starting value by an intermediate period in the absence of oxygen. A considerable reduction necessitates an intermediate period of several hours. (6) If, after a period of oxidation at constant pressure, the pressure is changed to a new constant value, the reaction rate changes very rapidly in such a way that it is greater the greater the new pressure and *vice versa*.

EFFECT OF SHEET THICKNESS ON ABSORPTION RATE

By considering conditions in a thin lamina parallel to the faces of a uniform sheet of rubber containing antioxidant and exposed to oxygen maintained at constant pressure, it may be shown that when the dynamic equilibrium state of absorption at a constant rate has been attained:

$$\frac{d^2c}{dx^2} = \frac{\sigma}{D} F(c)$$

where c = oxygen concentration at a distance x from either face of the sheet
σ = quantity of rubber in unit volume
D = diffusion coefficient of oxygen in the rubber
$F(c)$ = quantity of oxygen which reacts with unit quantity of rubber when oxygen concentration is maintained at c

By making assumptions as to the nature of the function $F(c)$, this equation may be integrated and the integration constants evaluated by using the conditions of symmetry about the center plane and of equilibrium between the oxygen in an infinitesimally thin surface film and the free gaseous oxygen[14]. The resulting relations can be used to determine the concentration gradient at the surface and, hence, the absorption rate. Guided by the results of the experiments described, it is tentatively assumed that reaction rate is directly proportional to oxygen concentration. This assumption leads to the following relation:

$$\frac{dQ}{dt} = kc_s \frac{\tanh \frac{\lambda X}{2}}{\frac{\lambda X}{2}}$$

where $\dfrac{dQ}{dt}$ = oxygen absorption rate

X = thickness of sheet

c_s = solubility of oxygen in rubber at external oxygen pressure

k = proportionality constant relation $F(c)$ and c

$\lambda^2 = \dfrac{k\sigma}{D}$

If ψ is defined as the ratio of the absorption rate of sheets of thickness X to that of the same quantity of the rubber in the form of infinitesimally thin sheets, it may be shown that:

$$\psi = \frac{\tanh \dfrac{\lambda X}{2}}{\dfrac{\lambda X}{2}}$$

This relation is applied to the particular cases of natural rubber specimens containing no fillers. Suppose that, at 40° C,

A_0 = absorption rate for infinitesimally thin sheets in grams oxygen per gram rubber per day at 1 atmosphere oxygen pressure, and

s = solubility of oxygen in the rubber in grams oxygen per cc. rubber per atmosphere oxygen pressure

By definition:

$$k = A_0/s$$

If we consider a specimen produced from a mixture such as the following, in parts by weight:

Rubber	100
Sulfur	3
Zinc oxide	5
Stearic acid	1
Accelerator	0.5

then we may put:

$$D = 0.231 \text{ sq. cm./day*}$$
$$s = 1.16 \times 10^{-4} \text{ gram/cc./atm.*}$$
$$\sigma = 0.89 \text{ gram/cc.}$$

Substituting these values:

$$\lambda = 182 \sqrt{A_0} \text{ cm.}^{-1}$$

$$\psi = \frac{\tanh 91X \sqrt{A_0}}{91X \sqrt{A_0}}$$

where X is measured in centimeters. Table VII gives the values of ψ for several values of A_0 and several values of X. It is evident that, even with the more rapidly oxidizing rubbers, sheets of substantial thickness give absorption rates closely approximating those for infinitesimally thin sheets. With slowly oxidizing rubbers the approximation is close for sheets of considerable thickness. Further subdivision of sheets into rods or cubes gives values for ψ still closer to unity than those shown in Table VII. The results of the experiments

* From unpublished work by the author.

TABLE VII

VALUES OF ψ FOR SEVERAL VALUES OF A_0^* AND X^*

	ψ				
X (cm.)	$A_0 = 10^{-2}$	$A_0 = 10^{-3}$	$A_0 = 10^{-4}$	$A_0 = 10^{-5}$	$A_0 = 10^{-6}$
1.0	0.11	0.35	0.79	0.97	1.00
0.75	0.15	0.45	0.87	0.99	1.00
0.5	0.22	0.62	0.94	0.99	1.00
0.25	0.43	0.97	1.00	1.00	1.00
0.1	0.79	0.97	1.00	1.00	1.00

* In grams of oxygen per gram of rubber per day at 1 atmosphere oxygen pressure.

recorded differ negligibly from those which would have been obtained by using infinitesimally finely subdivided specimens. In other words, oxygen concentration throughout the specimens was substantially uniform, so that the graphs of absorption rate against oxygen concentration would be of the same shape as those of absorption rate against oxygen pressure.

Confirmation of these conclusions was afforded by the results of an experiment in which the absorption rate of lightly masticated pale crepe rubber was determined using specimens in the form of cubes of about 3-mm. side and a cylinder of 1.4-cm. diameter and 25-cm. length. The determinations were carried out at 40° C with an oxygen pressure of 75.0 cm. of mercury under conditions of complete darkness. The equilibrium absorption rates were 1.32×10^{-5} and 1.39×10^{-5} gram oxygen per gram rubber per day, respectively. The good agreement shows that with both specimens oxygen concentration was substantially uniform throughout and that, at 40° C with specimens at least as great as the cylinder, diffusion is negligible as a rate-determining factor with this particular rubber.

DISCUSSION

The oxidation behavior of natural rubber in the absence of antioxidant is in agreement with the free-radical chain reaction theory for the oxidation mechanism of simple, unconjugated olefins proposed by Bolland and Gee[15], which was based on experimental work carried out chiefly on ethyl linoleate.

Sufficient data are not yet available for the extension and modification of this mechanism to include the oxidation behavior of rubbers in the presence of antioxidant. The attainment of a dynamic equilibrium oxidation state, however, suggests that an antioxidant produces its effect by controlling and maintaining at a low constant value the concentration of the first oxidation product, the hydroperoxide, ROOH[16] (where RH designates the rubber molecule, H being one of its α-methylenic hydrogen atoms), or the concentration of the free radicals R— and RO$_2$— to which it gives rise and which are responsible for chain propagation.

SUMMARY AND CONCLUSIONS[17]

Constant-pressure oxidation experiments on natural rubber in the absence of antioxidant confirm that the reaction is autocatalytic and essentially similar to that for the oxidation of simple, unconjugated olefins. The results are in accord with a free-radical chain reaction mechanism. In the presence of antioxidant at constant pressure, rubbers reach a dynamic equilibrium state of oxidation at a constant rate. This rate is greater, the greater the pressure, but increases less rapidly than pressure. Several graphs are given to show the

relation between equilibrium oxidation rate and oxygen pressure for several rubbers. If the pressure is reduced and again maintained constant after the attainment of the equilibrium oxidation rate at one pressure, the rate at the new pressure falls slowly over several hours from an initial high value to that consistent with the new pressure. This effect is more marked the less susceptible the rubber to oxidation.

Methods of investigating the rubber-oxygen reaction in which pressure is allowed to fall spontaneously as oxidation proceeds are experimentally shown to lead to erroneous conclusions. The reasons suggested for this are the autocatalytic nature of the reaction in the absence of antioxidants and the persistence of a high oxidation rate after a pressure reduction in the presence of antioxidant. An approximate relation is deduced between uniformity of oxidation, oxidizability, and specimen dimension for rubbers containing antioxidant.

ACKNOWLEDGMENT

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[17] Since the account of this investigation was written, a contribution to the literature by Shelton and Winn (*Ind. Eng. Chem.* **38**, 71 (1946)) appeared, which supports some of our conclusions. Working with GR-S in oxygen maintained at a more or less constant pressure of 1 atmosphere by periodic manual adjustment, they concluded: (1) in the presence of an antioxidant, GR-S attains a constant oxidation rate; (2) after the elimination of the antioxidant by oxidation, oxidation of the polymeric material becomes autocatalytic, and (3) except for high oxidation rates, diffusion of oxygen is not a rate-controlling factor with reasonably small specimens.

OXIDATION OF GR-S AND OTHER ELASTOMERS [*]

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The effect of heat aging on the physical properties of an elastomer is generally considered the result of oxidation, which produces both chain scission and cross-linking in the polymer. Early in the development of GR-S, a marked difference in the aging of GR-S and natural rubber vulcanizates was observed. From the effect of aging on hardness, tensile strength, modulus, and elongation[1] it appeared that cross-linking occurred more rapidly than chain scission with GR-S, but the reverse was true with natural rubber.

The work reported here was undertaken to provide a better understanding of the differences in aging of GR-S and natural rubber and to introduce new experimental methods for studying the mechanism of oxidation and antioxidant action in elastomers.

EXPERIMENTAL PROCEDURE

The synthetic polymers employed were prepared by emulsion polymerization, using hydroquinone as shortstop and phenyl-β-naphthylamine as antioxidant. For determination of infrared absorption spectra, with the exception of the sample used in Figure 3, the polymer hydrocarbon was isolated by precipitation of the crude polymer from benzene solution. The hydrocarbon in Figure 3 was isolated by alcohol coagulation of latex containing shortstop but no antioxidant.

Samples were aged in the form of thin sheets about 2–3 mm. thick. An ordinary air oven was used for air aging. For oxygen aging, samples were placed in a vacuum oven, the oven was evacuated, and oxygen was passed in until amospheric pressure was attained. Vacuum aging was carried out at about 20 mm. pressure in a vacuum oven which had been flushed out with commercial nitrogen. Traces of oxygen were present under these conditions.

Benzene solubility measurements were made by the static method. The oxygen uptake measurements were the difference between the oxygen content of the aged and unaged samples as determined by the method of Unterzaucher[2]. Determination of phenyl-β-naphthylamine was made by dissolving the acetone extract from a 5-gram sample of GR-S in 60 cc. of glacial acetic acid and titrating with 0.03 N sodium nitrite solution. The sulfonic acid and α-naphthylamine spot-test reagents, prepared according to the directions of Feigl[3], were used as an external indicator. The end point was taken as the point at which a pink color was produced within a few seconds after adding a drop of the solution to a spot-plate cavity containing one drop of sulfanilic acid reagent and one drop of α-naphthylamine reagent. In some cases the antioxidant was determined by a modification of the Kjeldahl method in which the ammonia was

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determined colorimetrically. Since 1 per cent antioxidant in GR-S is equal to only 0.064 per cent nitrogen, this modification was necessary to improve the sensitivity of the method.

Infrared absorption spectra were determined with a conventional Littrow type of rock-salt prism spectrometer. Samples were prepared by evaporation of a benzene solution of the polymer on a rock salt plate or in a steel frame floating on a mercury surface. The film thickness of samples prepared on salt plates was adjusted to give approximately 10 per cent transmission of the 1,450 cm.$^{-1}$ band. For the samples suspended on a steel frame, a film thickness of approximately 0.1 mm. was maintained by controlling the concentration and volume of the solution. To prevent undue oxidation the polymer film was dried under nitrogen. Since the film thickness of the samples in each series was kept approximately constant, a fair estimate of the intensity of absorption of a particular band can be made relative to a corresponding one of another sample without transforming the absorption curves into two terms of per cent transmission. The approximate slit widths employed are given in the following table:

Spectral region (cm.$^{-1}$)	Slit width (mm.)
800– 900	0.25
900–1200	0.17
1200–1900	0.12
1900–3700	0.06

EFFECT OF OXIDATION ON POLYMERS

Factors involved in the aging of GR-S and natural rubber would seem to be differences in the chemical reactivity of the polyisoprene and polybutadiene systems, —CH$_2$C(CH$_3$)=CHCH$_2$— and —CH$_2$CH=CHCH$_2$—, and variations in polymer structure, such as *cis-trans* isomerism, relative amount of '1,2- and 1,4-polymerization, and degree of branching. To determine the relative importance of chemical reactivity and polymer structure, a comparison was made of the effect of oxidation on uncured natural rubber and the following uncured emulsion polymers: polyisoprene, polybutadiene, isoprene-styrene in the ratio 75 to 25 and butadiene-styrene in the ratio 75 to 25. Table I shows the effect of heating these polymers at 125° C in an atmosphere of low oxygen content, in air, and in oxygen. Changes in benzene solubility indicate changes in the degree of cross-linking. For polymers which are completely soluble in benzene

TABLE I

EFFECT OF HEATING AT 125° C IN VACUUM, AIR, AND OXYGEN ON BENZENE SOLUBILITY AND INTRINSIC VISCOSITY OF POLYMERS DERIVED FROM ISOPRENE AND BUTADIENE

Polymer*	% Benzene solubility				Intrinsic viscosity			
	No heat-ing	30-hr. heating at 125° C in			No heat-ing	30-hr. heating at 125° C in		
		Vacuum	Air	Oxygen		Vacuum	Air	Oxygen
Natural crepe rubber	98	80	98	97	5.62	2.42	0.47	0.47
Polyisoprene	78	74	98	96	1.06	0.93	0.28	0.32
Isoprene-styrene, 75/25	71	69	90	95	1.33	0.83	0.47	0.33
Polybutadiene	85	39	39	53	..	..	..	..
Butadiene-styrene, 75/25	79	48	44	53	..	..	..	..

* Synthetic polymers contained 3 per cent phenyl-β-naphthylamine.

or become soluble on oxidation, the decrease in intrinsic viscosity indicates approximately the degree of chain scission.

On heating in a low oxygen atmosphere, the butadiene polymers exhibited a somewhat greater tendency to undergo cross-linking than did isoprene polymers. When heated in air or oxygen, all isoprene polymers underwent severe degradation or chain scission, as indicated by breakdown of gel and the low viscosity values. In marked contrast, however, the butadiene polymers exhibited a definite tendency to undergo further polymerization or cross-linking. Synthetic emulsion polymers are known to differ from natural rubber in structural features[4]. Since the net effect of oxidation on natural and emulsion isoprene polymers was chain scission, whereas cross-linking predominated with butadiene polymers, variations in polymer structure do not seem to explain the difference observed in the aging of GR-S and natural rubber. A difference in chemical reactivity of the polyisoprene and polybutadiene systems seems to be indicated. The observation that hydrochlorination and cyclization of isoprene polymers proceed much more readily than with butadiene polymers probably indicates that the presence of a methyl group increases the reactivity of the double bond. Farmer[5] suggested that the presence of an alkyl group on an ethylenic carbon atom has an activating effect on β-methylenic hydrogen atoms.

After the results given were obtained, a more detailed study was made of the effect of oxidation on the benzene solubility and intrinsic viscosity of uncured GR-S containing antioxidant. The results shown in Table II for the first sample were typical of many GR-S samples studied. The polymer remained completely soluble in benzene at the end of 20 hours of heating at 100° C. During this period the marked decrease observed in intrinsic viscosity indicated that chain scission was occurring more rapidly than cross-linking during the early stages of oxidation. Heating for periods greater than 30 hours resulted in a gradual decrease in benzene solubility. Thus, during the later stages of oxidation cross-linking occurred more rapidly than chain scission, with the formation of a gel fraction. The magnitude of the viscosity decrease and the time required for the appearance of gel varied somewhat for different GR-S samples, but no wide variations were observed.

Oxidation of GR-S samples containing gel resulted first in an increase in benzene solubility to a maximum solubility and then in a gradual decrease (Table II). Sample 2 became completely soluble after 10 hours of heating. Heating for more than 30 hours resulted in the appearance of a gel fraction. Sample 3 reached a maximum solubility of 72 per cent after 6 hours of heating, then gradually decreased in solubility. These observations are interpreted as a further indication that, during the early stages of oxidation, chain scission occurs more rapidly than cross-linking. However, during the later stages cross-linking becomes the more rapid reaction. The difference observed between samples 2 and 3 was attributed to a difference in degree of cross-linking of the gel fractions.

The effect of oxidation on the GR-S hydrocarbon, obtained by extraction of the nonhydrocarbon components, is shown in Table III. The rapid decrease in benzene solubility indicated the formation of a highly cross-linked polymer, but it was not possible to determine from the viscosity change whether a significant degree of chain scission had occurred. The sharp drop in viscosity at the gel point probably indicated that the fraction of high molecular weight had been removed from the soluble phase. Swelling index measurements, expressed as grams of benzene absorbed per gram of insoluble polymer, are a measure of the degree of cross-linking in the gel fraction. The gradual de-

TABLE II

EFFECT OF AIR OXIDATION AT 100° C ON GR-S CONTAINING 1.5 PER CENT
PHENYL-β-NAPHTHYLAMINE ANTIOXIDANT

	Hours at 100° C	% Benzene solubility	Intrinsic viscosity
Sample 1	0	100	1.70
	2	100	1.58
	4	100	1.55
	6	100	1.46
	10	100	1.34
	20	100	1.17
	30	98	1.10
	60	75	1.02
	90	60	0.82
Sample 2	0	79	1.81
	4	73	1.59
	6	91	1.74
	10	100	1.50
	20	100	1.20
	30	98	1.25
	50	74	0.57
	90	52	0.44
Sample 3	0	55	1.21
	4	65	1.06
	6	72	1.07
	10	51	0.75
	20	55	0.66
	30	45	0.67
	50	41	0.68
	90	35	0.57

TABLE III

EFFECT OF AIR OXIDATION AT 100° C ON GR-S HYDROCARBON

Hours at 100° C	% Benzene solubility	Intrinsic viscosity	Swelling index*
0	100	1.77	..
2	99	1.69	..
3	93	1.43	120
4	81	0.91	80
6	68	0.99	54
10	62	0.94	40
30	57	0.85	33
90	54	0.86	33

* Grams benzene absorbed per gram insoluble polymer.

crease observed in the swelling index was the result of further cross-linkage in
the gel fraction.

It is of interest to determine the amount of combined oxygen required to
bring about changes in the solubility and viscosity of the polymer.   Table IV

TABLE IV

OXYGEN UPTAKE DURING OXIDATION OF GR-S CONTAINING
PHENYL-β-NAPHTHYLAMINE ANTIOXIDANT (PBNA)

Hours at 100° C	Increase in % oxygen	% Benzene solubility	Intrinsic viscosity	% PBNA found
0	0	100	1.76	3.98
24	0.1	100	0.96	2.65
48	0.5	88	0.99	1.66
72	0.7	66	0.66	1.26
96	1.0	50	..	..
114	1.3	38	..	..

shows the changes in oxygen content, benzene solubility, intrinsic viscosity, and antioxidant content. The values recorded for oxygen uptake are probably accurate to about ± 0.1 per cent. An oxygen uptake of less than 0.5 per cent was sufficient to cause significant changes in the solubility and viscosity of the polymer. Oxidation caused a marked decrease in the antioxidant content. It appears that the amount of gel formed is roughly proportional to the amount of combined oxygen. This may be related to the observation of Shelton and Winn[6] that the increase in 200 per cent stress of GR–S during oxidation is roughly proportional to the amount of combined oxygen. Table V gives the

TABLE V

OXYGEN UPTAKE DURING AIR OXIDATION OF POLYMER HYDROCARBON
AT ROOM TEMPERATURE IN ABSENCE OF ANTIOXIDANT

Sample	Aging time (months)	% Oxygen found	Color of aged sample
GR–S 1	5	9.8	Yellow
GR–S 2	5	11.7	Yellow
Polybutadiene 1	27	15.0	Yellow-orange
Polybutadiene 2	27	15.8	Yellow-orange

oxygen content for GR–S and polybutadiene samples after aging at room temperature for long periods. These were highly purified samples of the polymer hydrocarbon and contained no antioxidant. The original samples were entirely colorless; the oxidized samples were colored yellow to yellow-orange.

These observations on the effect of oxidation on uncured GR–S indicate that both chain scission and cross-linking occur as the result of oxidation of the polymer. Except during the early stages of oxidation, the rate of cross-linking is more rapid than chain scission. Since aging properties are fundamentally related to the chemistry of the polymer hydrocarbon, the same reactions should occur during oxidation of vulcanized polymers, though probably at a different rate. In general this prediction is confirmed by the effect of oxidation on GR–S vulcanizates[7]. Although experimental studies of the effect of aging on physical properties are useful for practical purposes, they give little information as to the mechanism oxidation.

HYDROPEROXIDE THEORY OF AUTOXIDATION

The studies of Farmer and his coworkers[8] on the oxidation of simple olefins, such as cyclohexene, and more complex olefins, such as methyl oleate and natural rubber, indicated that the course of oxidation of unconjugated olefins may be represented as follows: Peroxidation takes place exclusively or almost exclusively at the methylene group adjacent to the double bond, with the formation of a hydroperoxide. Although the reaction probably has a free radical chain mechanism, the nature of the initiating step is not clear[9]:

$$—CH_2—CH{=}CH—CH_2— + \cdot OO\cdot \text{ (or } R\cdot) \longrightarrow$$
$$—CH—CH{=}CH—CH_2— + \cdot OOH \text{ (or } RH) \quad (1)$$

$$—CH—CH{=}CH—CH_2— + \cdot OO\cdot \longrightarrow —CH—CH—CH—CH_2— \quad (2)$$
$$\overset{|}{O}O\cdot$$

$$—CH—CH{=}CH—CH_2— + —CH_2—CH{=}CH—CH_2— \longrightarrow$$
$$\overset{|}{O}O\cdot$$

$$—CH—CH{=}CH—CH_2— + —CH—CH{=}CH—CH_2— \quad (3)$$
$$\overset{|}{O}OH$$

Termination of the reaction chain occurs by combination of the radicals involved in the propagation step.   Thermal decomposition of the hydroperoxide accelerates the reaction, probably by formation of a free radical capable of starting an oxidation chain.   Peroxide decomposition occurs side by side with peroxide formation.   This complex decomposition is not well understood, but, in general, the hydroperoxide group reverts to hydroxyl.   The active oxygen reacts mainly with double bonds to form epoxides.   There is some evidence that peroxide decomposition may also lead to the formation of carbonyl groups.

$$-\underset{\underset{OOH}{|}}{CH}-CH=CH-CH_2- \longrightarrow -\underset{\underset{OH}{|}}{CH}-CH-CH-CH_2- \tag{4}$$

$$-\underset{\underset{OOH}{|}}{CH}-CH=CH-CH_2- + -CH=CH- \longrightarrow$$

$$-\underset{\underset{OH}{|}}{CH}-CH=CH-CH_2- + -CH-CH- \tag{5}$$

In view of the important effect of chain scission and cross-linking on the physical properties of a polymer, the course by which these reactions occur is of particular interest.   The attempts which were made by Farmer and his coworkers[10] and also by Taylor and Tobolsky[11] to explain these reactions were directed along two somewhat different lines of thought.   The first theory assumes that both chain scission and cross-linking occur through reactions of the peroxide or its decomposition products.   The second theory considers that the role of oxygen is to form free radicals, which may disproportionate to cause chain scission or attack the double bond to bring about cross-linking.

Application of the hydroperoxide theory of oxidation to synthetic elastomers is complicated by the fact that polymerization of dienes usually occurs by both 1,2- and 1,4-addition to the conjugate system.   In the case of isoprene, 3,4-addition also occurs[12].   There is evidence that the C—H bond energy decreases in the order: primary > secondary > tertiary.   Further, the bond energy decreases when the hydrogen atom is attached to a carbon atom adjacent to the double bond[13].   On this basis oxidation of synthetic elastomers derived from butadiene and isoprene occurs at points in the polymer chains at which secondary or tertiary hydrogen atoms are adjacent to a double bond.   Such points are indicated by an asterisk:

BUTADIENE POLYMERS

$$-\overset{*}{C}H_2-CH=CH-\overset{*}{C}H_2- \qquad -\overset{*}{\underset{\underset{CH_2}{\overset{|}{\underset{CH}{||}}}}{C}H}-CH_2-$$

ISOPRENE POLYMERS

$$-\overset{*}{C}H_2-\overset{\overset{CH_3}{|}}{C}=CH-\overset{*}{C}H_2- \qquad -\overset{*}{\underset{\underset{CH_2}{\overset{|}{\underset{C-CH_3}{||}}}}{C}H}-CH_2-$$

Accordingly, in synthetic polymers derived from butadiene and isoprene, both secondary and tertiary hydroperoxides may be formed on oxidation. Milas and Surgenor[14] recently presented evidence that thermal decomposition of *tert*-butyl hydroperoxide occurs in the following manner:

$$(CH_3)_3COOH \xrightarrow{95-100°C} (CH_3)_3COH + O \tag{6}$$

$$(CH_3)_3COOH \xrightarrow{250°C} (CH_3)_3CO\cdot + \cdot OH \tag{7}$$

$$(CH_3)_3CO\cdot \longrightarrow (CH_3)_2C{=}O + CH_3\cdot$$

$$CH_3\cdot + \cdot OH \longrightarrow CH_3OH$$

The latter mode of decomposition seems to be a general reaction of tertiary hydroperoxides. George and Walsh[15] showed that the products obtained by oxidation of cyclopentane and cyclohexane derivatives at 80–100° C may be readily explained on the basis of the formation and decomposition of tertiary hydroperoxides. A similar decomposition of tertiary polymer peroxides may lead to chain scission and the formation of a ketone group:

ABSORPTION SPECTRA OF OXIDIZED POLYMERS

Experimental study of the mechanism of oxidation of GR-S and other butadiene polymers is made difficult by the fact that these polymers become insoluble as the result of oxidation. Since infrared absorption spectra can be readily measured on a thin polymer film, this method is of particular value in such cases.

The infrared absorption spectra curves shown in Figures 1 and 2 were obtained by heating production GR-S and the GR-S hydrocarbon at 105° C in an air oven and at 40° C in ultraviolet light (Atlas Fadeometer). These curves are plotted as transmission, measured as a galvanometer deflection, against frequency in wave number. The present infrared data were obtained with the object of studying the oxidation of unsaturated polymers from a qualitative standpoint.

The pronounced changes which occur in the spectrum of the GR-S hydrocarbon as the result of oxidation are shown in Figure 1. In general, new bands were found to appear at 890, 1,175, 1,720, and 3,600 cm.$^{-1}$, strong general absorption was observed in the region 1,000–1,300 cm.$^{-1}$, and a decrease in absorption occurred at 914 cm.$^{-1}$ The sample heated 20 hours at 105° C

FRESH SAMPLE

ULTRA-VIOLET ACTIVATED

HEATED AT 105° C.

FREQUENCY, CM.⁻¹
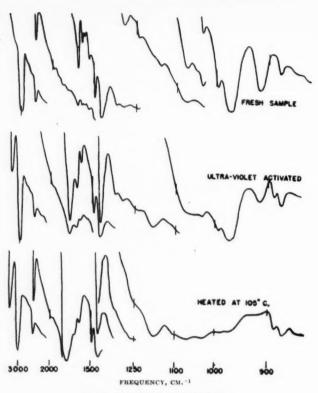
Fig. 1.—GR-S without antioxidant.

appeared to have undergone a much higher degree of oxidation than the sample heated 48 hours at 40° C in ultraviolet light.

The changes in the spectrum produced by oxidation of regular production GR-S containing phenyl-β-naphthylamine as antioxidant are shown in Figure 2. Heating for 20 hours at 105° C caused only slight changes in the spectrum. However, heating for 24 hours at 40° C in ultraviolet light brought about changes in the spectrum similar to those observed when oxidation was carried out in the absence of antioxidant.

Figure 3 shows the changes which occurred in the spectrum of the GR-S hydrocarbon during the early stages of oxidation. New bands appeared at 890, 1,700, 1,720, and 3,600 cm.⁻¹ after 2 hours of heating at 100° C. Further heating increased the intensity of the band at 3,600 cm.⁻¹ and the bands which first appeared at 1,700 to 1,720 cm.⁻¹ merged into one very intense band. This band extended from about 1,700 to 1,770 cm.⁻¹. General absorption began at about 1,000 cm.⁻¹ and gradually extended toward higher frequencies as oxidation proceeded. The intensity of the band at 914 cm.⁻¹ appeared to decrease more rapidly than the band at 970 cm.⁻¹; however, the general absorption occurring in this region was a complicating factor.

DISCUSSION

The band which appears at 3,600 cm.⁻¹ is associated with vibrations of the O—H group. The intense absorption at 1,700–1,720 cm.⁻¹ is undoubtedly

FRESH SAMPLE

ULTRA-VIOLET ACTIVATED

HEATED AT 105° C.

FREQUENCY, CM.⁻¹
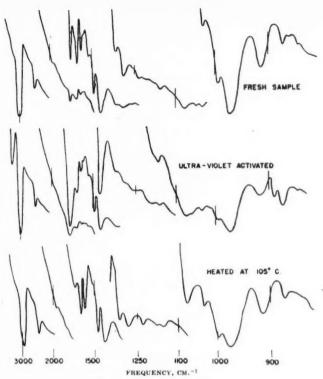
Fig. 2.—GR-S with antioxidant.

due to the presence of the C=O group, but it is difficult to determine the functional groups which may be involved. The frequency usually associated with the various carbonyl groups[16], is given as follows:

Monomeric acids	1770 cm.⁻¹
Esters	1750–1725 cm.⁻¹
Aldehydes and ketones	1725–1690 cm.⁻¹
Associated acids	1740–1700 cm.⁻¹

These characteristic frequencies are generally valid for the higher members of a homologous series. Conjugation, however, tends to lower the assigned frequencies. If it is assumed that any acid groups produced by oxidation of the polymer are distributed at random, an absorption band should appear at the position corresponding to the carbonyl band for monomeric acids at 1,770 cm⁻¹. The absence of this band during the early stages of oxidation would seem to indicate that no appreciable number of carboxyl groups are present. There seems to be some evidence that this band is present in the later stages of oxidation. Although the observed bands at 1,720 and 1,700 cm.⁻¹ are probably due to ketone or ketone and aldehyde groups, it is difficult to determine the significance of this doublet. This doublet may indicate that both aldehyde and ketone groups are presented, or that the frequency of part of the carbonyl groups has been shifted by conjugation. The fact that GR-S becomes yellow as the result of oxidation indicates the presence of conjugate carbonyl groups or carbonyl groups conjugated with double bonds. In either case a ketone car-

bonyl would be involved. Both the shape and the width of the band in the region 1,770–1,700 cm.$^{-1}$ suggest that several carbonyl groups are present in the later stages of oxidation. The bands at 996 and 914 cm.$^{-1}$ are attributed to side vinyl groups and the band at 967 cm.$^{-1}$ to the internal double bonds present in the polymer[17]. The decrease in intensity of the 914 cm.$^{-1}$ band indicates that double bonds are undergoing saturation or scission. The very intense, general absorption in the region 1,000–1,300 cm.$^{-1}$ is associated with vibrations of the C—O group and may be due to acid, ester, hydroxyl, or ether groups. No definite explanation can be offered for the appearance of a band at 890 cm.$^{-1}$, but olefins of the type $R_2C=CH_2$ have a band in this region.
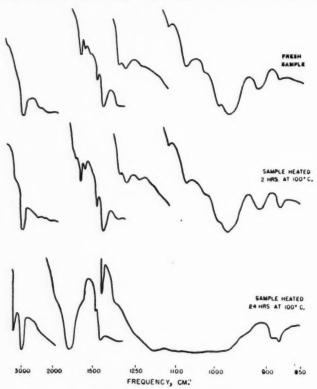
FIG. 3.—GR-S during early stages of oxidation.

Studies on the oxidation of GR-S and natural rubber showed that the concentration of peroxidic oxygen is never very high. Thus it is probable that the observed O—H absorption during the early stages of oxidation is due primarily to hydroxyl and not to carboxyl or hydroperoxide groups. Since thermal decomposition of hydroperoxides results in the formation of hydroxyl and ketone groups, the probable presence of these groups in oxidized GR-S is taken as an indication that the initial oxidation product is a hydroperoxide. Other functional groups containing oxygen seem to be indicated by the complex nature of the changes in the absorption spectra, but identification of these groups cannot be made with any degree of certainty on the basis of the present data. Since the C—O absorption bands for both alcohol and ether groups

generally occur in the same region, there seems to be little hope of establishing the presence or absence of either-type cross-links in oxidized GR-S. As already indicated, chain scission may result from peroxide decomposition, which leads to the formation of aldehyde and ketone groups. Although evidence for the presence of these groups has been presented, there does not appear to be much possibility of establishing the mechanism of chain scission by infrared methods alone.

Figures 4, 5, and 6 show the effect of oxidation on the spectra of the hydrocarbons derived from natural rubber, polyisoprene, and polybutadiene, respectively. The changes brought about by oxidation were similar to those
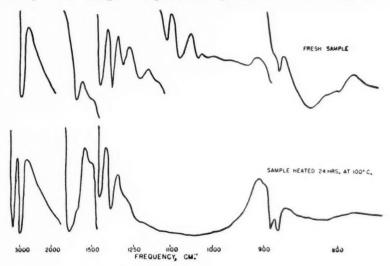
FIG. 4.—Hevea rubber changes on oxidation.
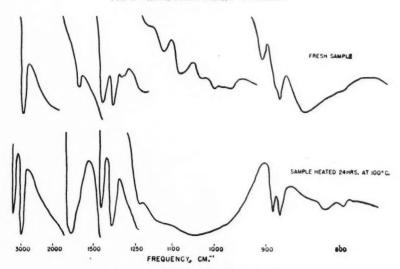
FIG. 5.—Polyisoprene changes on oxidation.
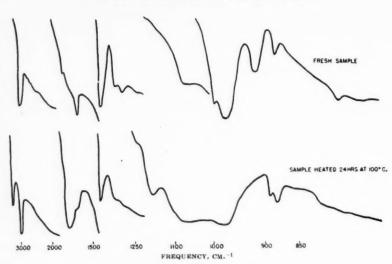
Fig. 6.—Polybutadiene changes on oxidation.

observed with GR-S. In the case of natural rubber and polyisoprene the decrease in intensity of the band at 840 cm.$^{-1}$ indicates saturation or scission of the double bonds in the polymer chain. On the basis of the changes in the infrared absorption spectrum, the mechanism of oxidation of all the elastomers studied appears to be similar.

MECHANISM OF ANTIOXIDANT ACTION

Aging of GR-S for 20 hours at 105° C in the presence of an antioxidant caused little change in the spectrum, whereas a similar aging period in the absence of an antioxidant brought about a marked change in the spectrum. In addition, the antioxidant provided much more effective protection against thermal oxidation than for oxidation catalyzed by ultraviolet light. These observations suggest that infrared methods may be of value in fundamental studies in the field of antioxidants.

There seems to be practically no data in the literature on the consumption of antioxidants during accelerated aging. Table VI shows the effect of air oven aging at 100° C on the phenyl-β-naphthylamine content of GR-S.

TABLE VI

EFFECT OF ACCELERATED AGING ON PHENYL-β-NAPHTHYLAMINE
CONTENT OF GR-S

Hours at 100° C	% PBNA in GR-S (Kjeldahl)	% PBNA in acetone extract		% PBNA in extracted sample (Kjeldahl)
		Nitrous acid	Kjeldahl	
0	1.43	1.36	1.35	0.15
24	1.42	0.75	..	0.37
48	1.29	0.36	..	0.61
96	1.32	0.12	..	0.88
400	1.45	0.02	0.22	1.01

Oxidation caused a marked decrease in the antioxidant content of the acetone extract. An appreciable quantity of the antioxidant appeared to combine with the polymer. In Table VI the column under nitrous acid refers to

the secondary amine content as determined by titration of the acetone extract with nitrous acid, assuming that phenyl-β-naphthylamine was the only secondary amine present.

Since phenyl-β-naphthylamine is not readily attacked by atmospheric oxygen at 100° C, either in the crystalline form or in toluene solution, it would appear that destruction of the secondary amine group may occur as a consequence of termination of the oxidation chain reaction. It is conceded that reaction of the antioxidant with polymer oxidation products may occur to some extent.

If oxidation involves a chain mechanism of the type indicated in reactions 1 to 3, it is suggested that the antioxidant may terminate the oxidation chain in the following way:

$$
\begin{array}{c}
\hspace{2.5cm} H \\
\hspace{2.5cm} | \\
-CH-CH=CH-CH_2- + C_{10}H_7-N-C_6H_5 \longrightarrow \\
| \\
OO\cdot
\end{array}
$$

$$
\begin{array}{c}
-CH-CH=CH-CH_2- + C_{10}H_7-N-C_6H_5 \quad (9) \\
| \hspace{4cm} \text{Radical A} \\
OOH
\end{array}
$$

Diarylamino radicals such as A do not react with oxygen. Because of resonance stabilization, such radicals are probably too inactive to start a new oxidation chain by removal of a hydrogen atom from the polymer.

ACKNOWLEDGMENT

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ACCELERATED AGING OF VULCANIZED RUBBER. FACTORS DETERMINING THE RELATION BETWEEN OVEN AND BOMB AGING *

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INTRODUCTION

It is well known that, in general, no two accelerated aging tests agree in indicating the relative rates of deterioration of different rubbers, and they may even arrange the rubbers in different orders of merit. Expressed in a different way, the ratio between the rates of deterioration produced by two aging tests may vary widely from one rubber to another. This is true even of tests involving the same deteriorating influences, e.g., the Geer oven and oxygen bomb, both of which depend on heat and oxygen.

Many examples of this can be found in the literature[1], but reference may be made to one particularly striking case, which, indeed, gave the incentive to the present investigation. In an examination of rubber gloves made by different manufacturers, it was found that the number of days' Geer oven aging equivalent to 1 day in the oxygen bomb varied from about 2 to 30.

In spite of the importance of these facts in the application of accelerated aging tests to rubber, little systematic study has yet been made of the way in which the relation between different aging tests depends on the composition and vulcanization of the rubber. It was with the object of elucidating this point that the present investigation was undertaken. The work is not yet complete, and the present report records the progress so far made.

EXPERIMENTAL

METHODS

The aging tests examined were the Geer oven (70° C) and oxygen bomb (70° C and 300 lbs. per sq. in.). As both tests use the same temperature, the factor responsible for the difference in aging rate is the concentration of oxygen.

The variables in the nature of the rubber were sulfur ratio, accelerator, and degree of vulcanization. All tests were made on dumb-bell specimens, Type B of B.S. 903—1940 (Figure 3), cut from press-vulcanized sheets 0.1 inch thick, and the technique of the aging and tests was generally as described in that specification.

The percentage fall in tensile strength during aging has been taken as the measure of deterioration, following the recommendation made as the result of previous studies of aging[2].

The oven and bomb aging curves for tensile strength did not generally differ radically in shape, but only in time scale, so it is possible to express the relative rates of deterioration with sufficient accuracy by a single value of the oven/bomb ratio, that is, the ratio between the oven and bomb aging periods that produce the same deterioration.

It must be borne in mind that estimates of the aging period for a given deterioration, and hence of the oven/bomb ratio, are subject to a fairly considerable experimental error. From the results of another investigation, in which the preparation and aging of the same mix was repeated 35 times, it can be deduced that if the oven/bomb ratios for two rubbers differ by less than about 35 per cent, they cannot with certainty be said to demonstrate a difference between the rubbers; even larger differences will occasionally be found between rubbers that should give similar results.

SERIES I

This series of experiments formed a comparison of high- and low-sulfur and sulfurless vulcanizates made from the mixes in Table 1.

TABLE 1

Mix:	A	B	C
Smoked sheet	100	100	100
Sulfur	6	2	—
Zinc oxide	5	5	5
Stearic acid	0.5	0.5	0.5
Tetramethylthiuram disulfide	—	0.25	3.0
Vulcanization			
Temperature (° C)	153	126	141
Periods (min.)	55	17	17
	80	25*	25*
	120*	40	40
Aging periods			
Geer oven (days)	1	6	35
	2	11	49
	4	16	63
	6	21	84
Oxygen bomb (hours)	3	48	96
	6	72	144
	12	96	192
	20	144	240

* Approximate optimum.

Figure 1 shows the decay of tensile strength during aging. All the curves are plotted with 5 days' oven aging equivalent to 24 hours' bomb aging. The high-sulfur mix A has aged particularly rapidly in the bomb, since the curves fall much more sharply than those for oven aging. With the accelerated low-sulfur mix B, the reverse is the case; for the sulfurless mix C, the two sets of curves seem to fall at about the same rate.

A study of the complete data indicates the following conclusions.

(1) Taking the results as a whole, the oven/bomb ratio does not change significantly as aging proceeds; that is, the oven and bomb aging curves do not differ radically in shape, but only in time scale.

(2) Increasing the period of vulcanization does not appreciably alter the ratio.

(3) Although both aging tests agree in showing A to age most rapidly and C most slowly, the oven/bomb ratio varies widely.

Mix	A	B	C
Mean ratio	12	2.2	4.5 (approx.)

(4) The above ratios do not fall in the same order as that of decreasing sulfur content, namely, A, B, C; this agrees with the conclusion, demonstrated by the experiments described below, that sulfur ratio is not the controlling factor in determining the relation between oven and bomb tests.
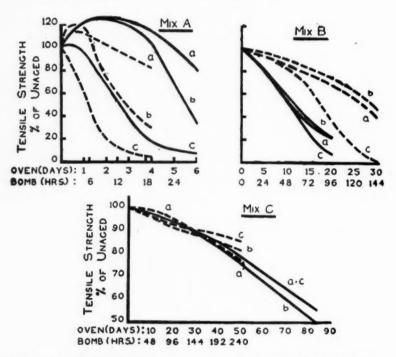
Fig. 1.—Aging curves for Series I (————— oven, - - - - - bomb; a, b, c on curves refer to the short, medium, and long vulcanization periods, respectively).

SERIES II

The object of these experiments was to examine the influence of sulfur content, nature of accelerator (or absence of same), and period of vulcanization. With each accelerator, two sulfur ratios were used, one being double the other, and each mix was vulcanized for two periods, in the ratio 2:3, estimated to be one on each side of the optimum. The base stock comprised rubber 100, zinc oxide 5, and stearic acid 1.5, to which sulfur and accelerator were added as shown in Table 2.

The aging periods (four for each rubber) had to be varied from one mix to another on account of their widely different rates of deterioration.

The average oven/bomb ratio for each rubber is shown in Table 3. It was again found that, in general, the ratio did not change significantly as aging

TABLE 2

Mix Nos.*	Accelerator	Sulfur		Vulcanization (min.)	
		Low	High	Low sulfur	High sulfur
1, 2	Mercaptobenzothiazole 0.75	2.0	4.0	30, 45	20, 30 at 141° C
3, 4	Butyraldehydeaniline 0.75	2.0	4.0	30, 45	20, 30 at 141° C
5, 6	Zinc pentamethylenedithiocarbamate 0.375	2.0	4.0	20, 30	13, 20 at 126° C
7, 8	Tetramethylthiuram disulfide 0.25	2.0	4.0	20, 30	13, 20 at 126° C
9, 10	Diphenylguanidine 1.0	2.0	4.0	30, 45	20, 30 at 153° C
11, 12	Litharge 7.0	3.5	7.0	20, 30	13, 20 at 153° C
13, 14	None	3.5	7.0	110, 170	75, 110 at 153° C

* The first and second numbers of each pair refer to low and high sulfur mixes, respectively.

TABLE 3

Mix No.	Accelerator	Period for 50% deterioration* (days)				Oven/bomb ratio*	
		Oven		Bomb			
		(a)	(b)	(a)	(b)	(a)	(b)
1	MBT	(110)	(65)	>2.5	(4.5)	—	14.3
2	MBT	64	48	>3.0	(4.3)	—	11.3
3	BA	37	21	3.2	2.2	11.8	9.6
4	BA	29	17	>2.5	2.15	—	7.8
5	ZPD	20	17	>2.5	>2.5(?3)	—	? 6
6	ZPD	12.5	12.5	3.4	(4.3)	3.7	2.8
7	TMT	16.5	13	3.0	2.1	5.7	6.2
8	TMT	16.5	14	3.0	3.4	5.6	4.2
9	DPG	13.5	12	0.85	0.53	16	23
10	DPG	19	15	1.0	0.62	18.5	24
11	PbO	9.1	5.9	0.49	0.26	18.5	22.5
12	PbO	15.5	4.4	0.59	0.25	26	17.5
13	None	7.4	<1	0.34	0.42	22	<2.4
14	None	6.8	<1	0.25	0.25	27	<4

* Columns headed (a) and (b) refer to the shorter and longer vulcanizing periods, respectively (see Table 2). Figures in brackets are extrapolated from the aging curves.

proceeded. To make the Table more informative, figures have been included for the aging period required to reduce the tensile strength by 50 per cent.

The following conclusions may be drawn from Table 3.

(1) With one important exception, increasing the vulcanizing period produces only small changes in the ratio, which, moreover, are not always in the same direction and are usually within the limits of experimental error. The exception is provided by the (b) vulcanizates of the unaccelerated mixes; these give very low ratios, owing to their deteriorating extremely quickly in the oven. This observation is in line with the reference by Jackson[3] to the "tendency for a slightly overcured nonaccelerated stock to be shown in a rather poor light" by the oven test. The reason for this exceptional behavior is not clear; it seems unlikely that it can be due to the fall in tensile strength on overvulcanizing, because 1 day at 70° C, which caused serious loss of tensile strength, should be equivalent only to 1 or 2 minutes' vulcanization at 153° C, assuming the normal temperature coefficient to be applicable.

(2) Doubling the proportion of sulfur, with the same accelerator, reduces the ratio somewhat in four cases and increases it in three; the average change, however, is small (a decrease of 15 per cent) and, in view of the experimental errors involved, cannot with certainty be claimed as a real effect.

(3) Mixes containing different accelerators differ widely in oven/bomb ratio, and indeed the nature of the accelerator seems to be the most important controlling factor.

(4) The oven and bomb tests do not arrange the mixes in the same order of age resistance; although both agree in showing Mixes 1 and 2 to be the best and 11–14 the worst, the order of merit among the remainder is different according to the two tests.

Conclusion (1) agrees with that from Series I above, except that it brings out a new point regarding overvulcanized unaccelerated rubbers. Conclusion (2) establishes definitely that the proportion of sulfur, within the normal limits of variation for soft rubber mixes, is not an important factor, though the small effect observed is in the expected direction, as will be shown later.

Conclusion (3) requires further consideration. The most obvious characteristic of an accelerator is the rate of vulcanization which it induces, and it is,
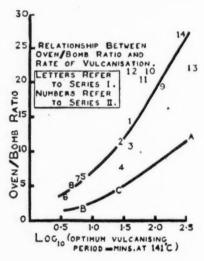
Fig. 2

therefore, of interest to see how this is related to the oven/bomb ratio. In Figure 2 the equivalent optimum vulcanizing period at 141° C is plotted (on a logarithmic scale for convenience) against the oven/bomb ratio for each mix, the average ratio for the two vulcanizates being taken, except with Mixes 13 and 14, where only the (a) vulcanizate is considered.

There is a clear tendency for the (numbered) points for Series II to lie on or near a rising curve; those for Series I lie along a similar curve, but lower on the graph. The reason why rapidly vulcanizing mixes give low ratios seems to be as follows. Deterioration of tensile strength of natural-rubber vulcanizates during accelerated aging results from both oxidation and overvulcanization. With a rapidly-vulcanizing mix the latter tends to predominate, and as its rate is controlled by the aging temperature, which is the same in both oven and bomb tests, the rates of deterioration tend to become the same, i.e., the oven/bomb ratio approaches unity.

Actually the relationships are more complex than this, because the rate of oxidation also must affect the oven/bomb ratio. Thus, among mixes having the same rate of vulcanization, one which oxidizes very slowly deteriorates chiefly by overvulcanization, again giving a ratio approaching unity, whereas one that oxidizes rapidly deteriorates chiefly by oxidative decay, and as this is undoubtedly hastened by increasing the oxygen pressure, the oven/bomb ratio is greater than unity. How much greater, however, it is difficult to say, for the relation between oxygen pressure and oxidative decay is not one of simple proportionality. Theoretical considerations[4] indicate that the velocity of the oxidation reaction is independent of the oxygen pressure, and that if deterioration occurs more quickly at higher oxygen pressures this must be due to oxidation occurring to a greater depth; this agrees with statements[5], that in the Geer oven oxidation may not occur uniformly through the specimen because the oxygen pressure is too low. These conclusions are difficult to reconcile with experimental data, however. Investigations of aging in relation to oxygen penetration[6] indicate that rubbers such as the present Mixes 3, 4, 5, 9, and 10, when aged as 2.5 mm.-thick specimens in air at 70° C, should oxidize uniformly; hence, if oxidation velocity is independent of oxygen pressure, should give an oven/bomb ratio of unity. Actually these mixes give ratios ranging from 6 to 20.

Whatever may be the theoretical interpretation, however, the undoubted fact that rubber does deteriorate more quickly at higher oxygen pressures justifies the conclusion that a rubber which oxidizes slowly and(or) vulcanizes quickly may be expected to give a low oven/bomb ratio, whereas one that oxidizes quickly and(or) vulcanizes slowly gives a higher ratio. This is, of course, only an approximate statement of the case, because it ignores certain other variables that must have some influence, namely: (1) rate of deterioration by overvulcanization is not simply proportional to rate of vulcanization as normally determined, because mixes differ in plateau characteristics; (2) rate of oxidative deterioration does not bear a constant ratio to rate of oxidation.

The data available do not provide any direct measure of rate of oxidation, or of the deterioration caused solely thereby. However, among rubbers having the same rate of vulcanization it may be assumed, as a broad generalization, that rapid deterioration denotes rapid oxidation, and this enables certain features of the results to be explained, e.g., (1) the fact that Mixes 1 and 3 have lower ratios than 12, with the same rate of vulcanization (see Figure 2), since the latter deteriorates more quickly; probably a similar explanation accounts for the whole group of points 9–14 lying above the trend indicated by points 1–8; (2) the fact that C, Series I, lies below the points of Series II, since it deteriorates more slowly than mixes with the same rate of vulcanization in the latter series; the low position of A and B may be due to the same cause.

The absence in general of any marked change in oven/bomb ratio with increasing period of vulcanization also seems in accord with the hypothesis. There is ample evidence from the present results and other investigations[7] that oxidation of natural rubber is more rapid when it is more fully vulcanized. Such a rubber, however, would also deteriorate more quickly due to overvulcanization during aging. As increased rates of oxidation and overvulcanization react in opposite ways on the oven/bomb ratio, it is not surprising that the ratio is found not to show any marked change.

The effect of using more sulfur in the mix can also be predicted, because it increases the rate of vulcanization by about 40 per cent on the average, and as

there is no evidence that oxidation is accelerated, a decrease in the oven/bomb ratio would be expected. The observed effect is in this direction, although in itself not significant owing to the large experimental error involved.

Unfortunately, from the point of view of analyzing the results, the two factors that lead to low oven/bomb ratios, *i.e.*, rapid vulcanization and slow oxidation, tend to be associated together in the present mixes, since the rapidly-vulcanizing mixes often deteriorate (and hence presumably oxidize) most slowly, and *vice versa*. This makes it impossible to assess the effects of each of these factors separately. The following considerations, however, show that the rate of vulcanization must have an important direct influence, quite apart from any relation to oxidizability. If published values for the temperature coefficient of vulcanization can be assumed to hold down to 70° C (this is the case at least with unaccelerated mixes[8]), rapidly-vulcanizing mixes such as Mixes 7 and 8 must have received at least 10 times the optimum vulcanization during heating at 70° C for 15 days, which is the average oven aging period for these mixes in Table 3. Such violent overvulcanization must considerably lower the tensile strength of all but the most exceptional mixes. On the other hand, very slowly vulcanizing mixes like 13 and 14 do not become appreciably overvulcanized in either aging test, and the same is true of the moderately slow mixes like 9–12 in the bomb test.

Several published comparisons of oven and bomb aging have been studied to see whether they agree with the views discussed above. Unfortunately no satisfactory data relating to the effect of vulcanizing rate have been found, though a very low ratio (2.1) has been recorded for a rapidly vulcanizing "super-aging" mix[9].

The increased rate of oxidation caused by adding copper stearate to various mixes was found[10] in almost every case to increase the oven/bomb ratio, as expected, and the same is found in other experiments[11] with copper, ferric, and mercuric stearates, cupric chloride, and manganese oleate. In a comparison of diphenylguanidine and litharge mixes[12] the quicker deterioration of the latter, which seemed definitely to indicate quicker oxidative decay, was accompanied by a higher oven/bomb ratio.

On the other hand, antioxidants do not always produce the expected decrease in the ratio. In some cases the decrease is observed[13] and the more effective antioxidants produce the greater effect[14], whereas in other cases there appears to be no effect[15] or even an increase[16]. This might arise, however, from the antioxidant being rapidly oxidized and destroyed in the bomb test, an effect already discussed[4], thus increasing the oven/bomb ratio. It may be noted, moreover, that the slow oxidizing, antioxidant mixes of Booth[17] almost all give low ratios (about 3 or 4), as expected, and that among the mixes studied by Jones and Craig[10] the ratio varies between about the same limits as in the present investigation, *i.e.*, from 3, for the slowest-aging rubbers, to 20 for those that age most rapidly.

USE OF OVEN AND BOMB TESTS

The results described above show that, in attempting to estimate the relative lives of two rubbers, it is by no means immaterial which form of aging test is used, because if they differ markedly in rate of vulcanization or oxidizability, the two tests cannot be expected to agree. The discrepancy may be serious; thus, according to the oven test Mixes 6 and 9 have about the same life, but in the bomb test Mix 6 lasts nearly six times as long as Mix 9.

The question therefore arises, which test most nearly duplicates natural aging, that is, storage at normal atmospheric temperature in absence of light, strain, oil, grease, and the like, but it is not possible to give a definite answer on the basis of the present results. The view has been expressed[3] that the oven test, by increasing the temperature, but not the oxygen concentration, over-emphasizes after-vulcanization. This is not necessarily true, however; if oxygen diffuses into the rubber quickly enough to maintain uniform oxidation throughout, which certainly can be the case, and if oxidation and vulcanization have the same temperature coefficient between room temperature and 70° C, the Geer test must accelerate both oxidation and after-vulcanization equally. Actually, equality of the two coefficients seems unlikely since published values for the temperature coefficient of vulcanization vary at least between 1.76 and 2.84 per 10° C (see e.g., ref. 16), and coefficients of 2.38 and 2.50 for oxidative decay have been recorded[18]. According to these figures, indeed, the oven test could either under- or over-emphasize after-vulcanization. Whether the increased oxygen pressure in the bomb test can further accelerate oxidative decay and so over-emphasize this type of deterioration is not clear.

The present results do, however, confirm and emphasize the view expressed by previous workers that the utility of accelerated aging tests is limited to comparisons between rubbers of similar type, if accurate and reliable conclusions are to be obtained. Further, it is now possible to state what are the main factors whose variation may render comparisons between different natural rubber vulcanizates unreliable, namely, rate of vulcanization and oxidizability.

The results demonstrate also the danger of attempting to use a general conversion factor for converting oven to bomb aging periods or *vice versa*, a practice liable to introduce grave errors. The same must be said of the use of such factors for interconverting natural and accelerated aging periods.

SUMMARY

A study has been made of the influence of the following factors on the relative rates of tensile deterioration of natural rubber vulcanizates in the Geer oven and oxygen bomb, both at 70° C: period of vulcanization, sulfur ratio, nature of accelerator.

Expressing this relation as the *oven/bomb ratio*, i.e., the ratio between oven and bomb aging periods that give the same deterioration, the following conclusions are drawn.

(1) Varying the period of vulcanization of a given mix over a moderate range (2:3) around the optimum does not noticeably alter the oven/bomb ratio, except in unaccelerated mixes, where overvulcanization gave an abnormally low ratio, owing to the rubber perishing very rapidly in the oven.

(2) The effect of varying the sulfur ratio within the usual limits for soft rubbers is small, and appears to result from the quicker vulcanization of the mixes richer in sulfur.

(3) The nature of the accelerator profoundly affects the ratio, values ranging from 3 to 27 being found among the present mixes; this effect is believed to be exerted through the influence of the accelerator both on rate of vulcanization and on the oxidizability of the vulcanizate.

Theoretical considerations indicate that a rubber which vulcanizes quickly and(or) oxidizes slowly should give a low oven/bomb ratio, whereas one that vulcanizes slowly and(or) oxidizes quickly should give a higher ratio. The

experimental data are generally in accord with this, and there is evidence that both rate of vulcanization and oxidizability can have an important effect, but the data do not enable the separate effect of each to be assessed exactly.

The bearing of the results on the use of the oven and bomb tests is briefly discussed. It is shown that they demonstrate the fallacy of using a single factor for converting oven to bomb aging periods or *vice versa*, and that the relative natural aging resistances of widely different vulcanizates cannot be reliably assessed by either test, a limitation arising from the fact that the relative importance of oxidative decay and aftervulcanization varies from one type of mix to another, and that the temperature coefficients of these processes are not necessarily the same.

These facts are very important in relation to the choice and application of accelerated aging tests for specification purposes, since these usually have to be applied to rubbers of unknown compositions, which are likely to vary widely in their relative response to different aging conditions.

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THE POSSIBILITY OF TRANSFORMING
RUBBER INTO AN ION EXCHANGER *

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INTRODUCTION

Before taking up the actual subject of the present work, it is well to point out what is meant by an exchange of ions and to define an ion exchanger.

An exchange of ions is a chemical reaction which takes place in a heterogeneous medium; when a solid heteropolar substance is immersed in a liquid, usually aqueous, ions belonging to the solid pass into the liquid in exchange for ions of the same polarity in solution in the liquid, and these dissolved ions thereby become fixed on the solid substance in place of the ions which the latter has just given up. As an example, minerals of the type of zeolite (green sand, harmatome, chabasie, etc.) can exchange their alkaline-earth metal ions, i.e., their cations, for sodium ions in an aqueous solution of sea salt which wets them or penetrates through them, and this phenomenon is reversible. Such a reaction is the basis of the detartarizing purification of industrial waters containing lime.

Likewise the heteropolarity of exchangers sometimes renders their anions mobile, i.e., some substances give up their anions to liquids which wet them in exchange for the anions of these liquids, which thereby replace the anions liberated from the solids.

An ion exchanger is, then, an insoluble solid substance, which is an acid or one of its salts when the substance acts as an exchanger of cations, and which is a base or one its salts when the substance is an exchanger of anions[1].

However, not all bases which are insoluble in water are necessarily anion exchangers, nor are all acids which are insoluble in water cation exchangers. Although, for example, solid fat acids are definitely acidic and insoluble in water, they are not ion exchangers, for they lack one essential characteristic, viz., wettability, i.e., the existence of any considerable interfacial tension between them and the aqueous liquid with which they are in contact. Now it is the interfacial tension which sets up, in the zone of contact between liquid and solid, an "aureola" of high pressure in which the reaction involving an exchange of ions take place. Because of the pressure which prevails in this zone, reactions which involve a diminution in volume are the ones which take place in accordance with the law of Le Chatelier, providing however that other physico-chemical influences are not dominant.

The products of the exchange reaction diffuse rapidly in the aqueous medium and slowly into the interior of the solid substance until equilibrium is attained. This equilibrium is governed by the solubility quotient of the two insoluble substances which are present, one of which is the same ion exchanger that it was before the reaction, the other an ion exchanger after it has come in contact with the ionized salt solution[2].

Accordingly a cation exchanger may be defined as an insoluble acid with good wetting power, utilized in the free state or in the form of one of its salts; or, in the case of an anion exchanger, as an insoluble base also with good wetting power and utilized as such or in the form of one of its salts.

In recent times, these substances have found wide industrial applications, particularly in the preparation of pure water for accumulators, high-pressure boilers, in the chemical and pharmaceutical industries, etc.

An exchange of ions[3] takes place also in reactions connected with the fertility of soils[4] and with dyeing processes[5].

ANION EXCHANGERS AND RUBBER

The present paper describes experiments which were undertaken with the object of obtaining an ion exchanger from rubber by transforming the latter into an insoluble base or salt of a base. Later it is intended to study the transformation of rubber into a cation exchanger.

The few anion exchangers known at the present time are all macromolecular substances, as is rubber itself. This large size of molecule is one assurance among others of the insolubility of these substances. The first substance of this type which was studied in an exact way was aniline black. It is in the work of Stadnikoff[6], carried out in 1922, that there appears for the first time the word *exchange*, in combination, however, with adsorption, which obviously plays only a secondary role in the reaction[7]. Stadnikoff showed that aniline black, prepared in accordance with the method of Willstaetter and Dorogi and transformed into its base, can capture and exchange acids by giving up OH ions or other ions to anions in the solution which wets it.

It was attempted to prove that this reaction conforms to the law of Henry. It was found[8] that, like all other reactions involving an exchange of ions, it follows the extraction law of Berthelot, in which the solvent which is not miscible with water is the ion exchanger and the product which is distributed between the two "solvents" is the exchanged ion[9]. Henry's law agrees very well with the formulas which can be derived from this interpretation[10]. Other large molecules have likewise been employed as anion exchangers, notably synthetic resins having a basic reaction, such as aminoplasts[11].

These two types of substances have, however, certain disadvantages, particularly the second type, which are not in all cases completely insoluble. This is the reason that, in Germany, the great industry engaged in the manufacture of chemical products made efforts to improve them, and recommended the use of aminoplasts based on polymerized aromatic biguanides or on polymers of polyimines[11].

In view on the one hand of the macrostructure of rubber and, on the other hand, of the fact that the introduction of basic groups into insoluble substances has already been shown to be a method for obtaining ion exchangers[12], as, for example in the case of aminopolystyrene[13], the possibility of fixing basic groups on the rubber molecule as a means of preparing insoluble macromolecular bases was considered. The wettability of rubber, *i.e.*, its surface tension with respect to water, seemed sufficient provided that it would not be lowered too much by the introduction of the basic groups. *A priori*, this seemed improbable, since the opposite effect is usually found, for compounds of the constitution RNH_2 are ordinarily more soluble than those of the constitution RH; *e.g.*, aniline is more soluble than benzene, naphthylamines than naphthalene, cyclohexylamine than cyclohexane, etc.

At first view the introduction of basic groups into the rubber molecule seemed to be easy, but it will be shown that this is far from true. As a matter of fact, the vulcanization of rubber with various amino derivatives has already been studied, and it was hoped to take advantage of the results obtained, particularly those of Fisher, who carried out some interesting reactions between rubber and quinoneimines. Nevertheless the literature lacks information on the chemical behavior of the products obtained, especially with respect to their polarity; in fact the products have been studied chiefly from the point of view of their ordinary applications in the rubber industry, in other words, from the point of view of their mechanical properties and their oxidizability[14]. Data on their nitrogen content were scarce, and no data at all were available on their basicity, which is the feature of particular interest in the present study.

Experiments were therefore carried out with a view to determining whether it is possible to fix basic groups on the rubber molecule and thus to make the latter somewhat basic, without at the same time making it soluble in water or in dilute acids, and with the added possibility of rendering it granular. No attention was paid to mechanical strength, elasticity, or oxidizablity.

BASIS OF THE EXPERIMENTS

Four different methods were tried in attempts to fix basic groups on rubber.

(1) Introduction of a phenylamine group by reaction of an active methyl group, as is present in isoprene, with a nitroso group. This reaction is a well-known one in the chemistry of aromatic compounds, notably in dye chemistry, e.g., in the phthalocyanine series[15]:

(2) A synthesis reaction[16] by means of azo compounds, whereby it was expected that there would be simultaneous opening of the double bonds:

(3) The action of nitro groups, with fixation of an aromatic residue, in which it was hoped that there would be more or less extensive reduction:

(4) Finally, the method of Fisher, *i.e.*, the reaction of rubber with quinone-imines[17]:

$$H_3C-\underset{R_2}{\overset{R_1}{C}} + \text{(ring NH/NH)} + \underset{R_2}{\overset{R_1}{C}}-CH_3 \longrightarrow H_3C-\underset{R_1}{\overset{R_1}{C}}-NH \text{...} NH-\underset{R_2}{\overset{R_1}{C}}-CH_3$$

The first two of these methods gave no results; however, the experiments are described briefly in the "Experimental Part" because of a certain amount of light which they throw on the reactivity of the rubber molecule.

The third method showed that rubber can be vulcanized to a certain extent by the action of nitro compounds alone, without the addition of any accessory agent, with formation of compounds of the II type (see above).

Only the fourth and last method, adapted and modified to the needs of the present investigation, gave positive results. Here too it was necessary to employ complex insoluble quinoneimines to obtain an insoluble derivative of rubber which had at the same time a basic reaction.   Furthermore, it could not be proved definitely whether this basic reaction was not attributable to the complex quinoneimines merely functioning as filters in the rubber, although this seemed highly improbable, for in every case the rubber was definitely vulcanized, probably as a result of the oxidizing effect of the polyquinone-imines[18], particularly in those cases where the oxidation potentials had been found by Green and his collaborators[18] to be comparable to the oxidation potential of lead peroxide.

EXPERIMENTAL PART

REACTION BETWEEN RUBBER AND p-NITROSODIMETHYLANILINE

Theoretically the following reaction of the methyl group in the rubber molecule should be possible:

$$RCH_3 + ONC_6H_5N(CH_3)_2 \longrightarrow RCH:NC_6H_5N(CH_3)_2$$

such as takes place for example, between propenylbenzene and *p*-nitrosodimethylaniline, with formation of a basic insoluble resin:

$$C_6H_5CH=CHC\overset{H}{\underset{H}{\diagup}}\overset{H}{\diagdown} \quad O:NC_6H_5N(CH_3)_2$$

The same result is obtained by the reaction of cinnamic aldehyde and *p*-aminodimethylaniline:

$$C_6H_5CH=CHCH:O + H_2:NC_6H_5N(CH_3)_2 \longrightarrow C_6H_5CH=CHCH=NC_6H_5N(CH_3)_2$$

This condensation product polymerizes by means of the carbon-carbon double bond conjugated with that of the azomethine group, —CH=N—.

In the case of rubber, such a reaction takes place at 125° C and above, with a certain violence.   At the same time complete rupture of the rubber molecule

takes place, with formation of a basic resin, the hydrochloride of which is soluble in water. Among the reaction products, tetramethylbenzidine was isolated, and when the reaction was carried out at 150° C, evolution of nitrous vapors was observed; this would lend support to the view that tetramethylbenzidine is a product of the reaction.

In the presence of sulfur and with times of vulcanization ranging from one to three hours, with slow rise up to 145° C, more or less elastic products were obtained, progressing, with increase in sulfur content, to the state of ebonite. On treatment in granular form with dilute acids, the formation of derivatives of p-aminodimethylaniline and a little methylene blue was detected. However, it was not possible to prove the fixation of nitrogen with basic character on the rubber molecule.

REACTION OF RUBBER WITH AZO COMPOUNDS

By the action of chrysoidine there was neither vulcanization nor any fixation of nitrogen. At 145° C and in the presence of various proportions of sulfur, vulcanizates were obtained, the elasticity and strength of which depended on their sulfur contents. The chrysoidine which had been added was converted into a black resin, soluble in dilute acids, and no nitrogen was fixed on the rubber molecule.

REACTION OF RUBBER WITH NITROAMINE COMPOUNDS

It was attempted to vulcanized rubber with p-nitroaniline, with and without addition of sulfur and accelerator.

The most interesting result from the point of view of the chemistry of rubber was the obtaining of a small amount of a vulcanizate containing neither sulfur nor nitrogen. When mixtures of rubber and p-nitroaniline, containing no sulfur or other accessory agent, were heated from one to two hours at 145° C, a yellow rather pasty mass was obtained, which was partly soluble in benzene and in toluene. The undissolved residue contained the amine added, part of which had been transformed into p-azoxyaniline. By treatment of this residue with methanol to remove aromatic amino compounds, there remained a nervy material, which was insoluble in benzene or in toluene, and which could not be plasticized by milling. It was a form of vulcanized rubber containing no nitrogen nor obviously any sulfur, since none of the latter had been added.

It would appear, therefore, that the process involves, at least in part, the following reaction:

$$
\begin{array}{c}
\text{RH} \\
| \\
\text{C}-\text{CH}_3 + \text{O}_2\text{NC}_6\text{H}_4\text{NH}_2 \\
\| \\
\text{R}'_2
\end{array}
\longrightarrow
\begin{array}{c}
\text{R}-\text{R} \\
| \quad | \\
\text{H}_3\text{C}-\text{C} \quad \text{C}-\text{CH}_3 + \text{O} \\
\| \quad \| \\
\text{R}' \quad \text{R}'
\end{array}
\begin{array}{c}
\diagup \text{NC}_6\text{H}_4\text{NH}_2 \\
| \\
\diagdown \text{NC}_6\text{H}_4\text{NH}_2
\end{array}
$$

However this may be, the vulcanizate formed in the process was not the type of product sought, which was one with nitrogen-containing groups in the rubber molecule.

REACTION OF RUBBER WITH QUINONEIMINES

As the result of various unsuccessful attempts, the following procedure was finally developed.

A quinoneimine, $C_{48}H_{34}N_8 \cdot HCl$, was first prepared by oxidizing aniline hydrochloride with a concentrated solution of ferric chloride at a low tempera-

ture.   The product, which was insoluble in water, acids and alkalies, but slightly soluble in morpholine, contained two quinoidine groups.   After having been washed with acid, it was treated with boiling ammonium hydroxide to eliminate all traces of chloride ions; then was washed, and finally was dried at 120° C.

This product (75 parts) was mixed into rubber (22.5 parts) and lead peroxide (2.4 parts), and the mixture was heated in a mould for 2 hours at 145° C. The resulting product, which had the character of leather, was insoluble in benzene and in toluene.   It was reduced to granular form, was washed with a mixture of benzene and formic acid, then with acetic acid to eliminate lead, and finally with water until neutral.   It still contained a certain percentage of nitrogen which could not be removed by washing with very dilute hydrochloric acid or sulfuric acid.

After treatment with these acids and then washing with hot water until neutral, the product had the character of an ion exchanger.   It was insoluble in water and in weak acids; it contained 9.7 per cent of nitrogen, it had good wetting power, *i.e.*, an interfacial tension[19] of 41 dynes per cm., and removed very effectively the acidity of solutions of dilute acids.   When employed in the form of a salt, it tended to displace the acid constituents of salts in aqueous solutions.   Like all weak bases, however, it was sensitive to hydrolysis.

Its properties were equally like those of the quinoneimine which had served as vulcanizing agent, except for its surface tension, which was almost twice that of the quinoneimine itself.   Nevertheless, in view of the small proportion of rubber in the product, there still remained some doubt as to the origin of the properties of an ion exchanger.   Yet even after swelling in benzene, there was no appreciable solution in morpholine, a typical solvent of the quinoneimine employed in the reaction.

It would seem, then, that the product in question is an amino derivative of rubber, vulcanized according to the method of Fisher without sulfur but, in the presence of lead peroxide, with complex, water-soluble quinoneimines.

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ALKYLPHENOL SULFIDES AS
VULCANIZING AGENTS *

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Three of the major problems involved in the utilization of the butadiene copolymers of styrene or acrylonitrile are the deficiency of tackiness in these polymers, the exacting control of vulcanization that is usually required, and the retention of original properties on aging. Considerable time and effort have been expended in trying to improve the tackiness of these polymers. Particular emphasis has been placed on the effect of addition of organic materials to these synthetics for the improvement of their tackiness characteristics. An examination of a large number of organic agents revealed that alkylphenol sulfides are effective materials for imparting building tackiness to the butadiene copolymer types of synthetic rubber.

When properly reinforced and cured with sulfur and organic accelerators, the butadiene copolymers of styrene (GR-S) or acrylonitrile (Buna-N) possess physical properties approaching those of natural rubber vulcanizates. Vila[1] states that the phenomenon of reversion of natural rubber does not exist in the case of the butadiene copolymers. Unlike the vulcanizates obtained from natural rubber, vulcanizates of butadiene copolymers become progressively stiffer with overcuring when a normal type of acceleration is employed. A sensitive index of this stiffening effect is represented by an increase in modulus, sometimes termed "marching modulus", and a decrease in elongation of these butadiene copolymers with aging. It will be shown that alkylphenol sulfides moderate this stiffening effect when used as vulcanizing agents and, in so doing, extend the useful life of the vulcanizate.

Considerable attention has been given to the effect of acceleration as a means for improving the vulcanizates of these polymers. Innumerable variations of the accelerator problem have been studied. In connection with this problem rubber technologists have investigated many types of accelerators, the amount of acceleration, combinations of accelerators, and sulfur-bearing accelerators, as well as the ever-important question of sulfur-accelerator ratio.

However, not as much interest has been shown in regard to the use of new types of vulcanizing agents. Sturgis, Baum, and Vincent[2] reported that polynitrophenols improve the aging characteristics of GR-S vulcanizates. Poor dispersion of sulfur was postulated as one of the possible causes of irregularities in the stress-strain data of butadiene vulcanizates. Rostler and Mehner[3] dissolved sulfur in Naftolen, an unsaturated hydrocarbon composition, and used this mixture as a source of sulfur for obtaining good dispersion in Buna-N vulcanizates. Several years ago the Thiokol Corporation introduced a vulcanizing agent called VA-2, which was a master batch of a sulfur-bearing material containing 25–30 per cent available sulfur[4].

Alkylphenol sulfides are compatible with, and in most instances soluble in, butadiene rubbers, and therefore are readily incorporated into the stock in standard mixing equipment. These aromatic sulfides exert a smoothing-out effect in butadiene copolymers during mixing, and aid in the dispersion of the pigments. Furthermore, this type of sulfide, properly selected and used, acts as an effective vulcanizing agent for butadiene copolymers. According to patent literature, alkylphenol sulfides[5] as well as phenol sulfides[6] have been used in rubber for a variety of purposes—for example, antiflexing agents, stabilizers, antioxidants, and age-resisters. The use of these materials as vulcanizing agents, however, is apparently new.

Several attempts were made to elucidate the mechanism of vulcanization by alkylphenol sulfides. An examination of the acetone extract from a GR-S stock vulcanized with p-tert-amylphenol disulfide gave no evidence of free alkylphenol or the sulfide. From these facts it may be inferred that the entire alkylphenol sulfide molecule enters into the vulcanization reaction. This type of organic compound apparently contains labile sulfur which is readily available for vulcanization and consequently serves as a primary vulcanizing agent.

ALKYLPHENOL SULFIDES

Alkylphenol sulfides are dark amber or brown and range from viscous liquids to hard, brittle resins. A variety of different compounds exist which exhibit variations in the number, position, length, and configuration of the alkyl group or groups, as well as in the sulfur content. A representative formula of the alkylphenol sulfide type of compound is:

S_x IS $-S-$ $-\overset{\overset{\textstyle S}{\|}}{S}-$ $-S-S-$, ETC.

R & R´ = IDENTICAL OR DIFFERENT ALKYL GROUPS

R´´ = HYDROGEN OR ALKYL GROUP

The sulfur may be present in the form of a mono-, di-, or poly-sulfide, with the possibility of a double sulfur bridge being formed between two phenol molecules. These possible variations afford numerous combinations for producing different alkylphenol sulfides. As might be expected, the improvement in the tackiness of butadiene copolymers and the physical properties of the resulting vulcanizates depend a great deal on the particular alkylphenol sulfide employed.

Some twenty-five different alkylphenol sulfides were evaluated in GR-S with respect to their tackiness imparting qualities and their merit as vulcanizing

agents.   In these tests a ratio of 5 parts of alkylphenol sulfide per 100 parts of rubber was used as the minimum amount of material which would impart tackiness and appreciable improvement to the synthetic.   Inasmuch as these materials are vulcanizing agents as well as tackifiers, due consideration must be given to the amount of elemental sulfur used in the compound.   Therefore, to produce a satisfactory vulcanized product, neither the tackiness-producing property of the alkylphenol sulfide nor its activity as a vulcanizing agent can be considered separately.

To investigate the behavior of the alkylphenol monosulfide as vulcanizing agents, *p-tert*-amylphenol monosulfide of 12.8 per cent sulfur content was prepared and its activity in GR-S studied.   One mole of sulfur dichloride, 100 per cent pure by chemical analysis, was reacted with $1\frac{1}{3}$ moles of *p-tert*-amylphenol to produce a pure monosulfide.   A portion of this material was treated with potassium cyanide in alcoholic solution to remove any labile sulfur, uncombined sulfur, or sulfur in the disulfide form.   Both the original monosulfide and that purified by potassium cyanide treatment analyzed within a few tenths of a per cent of the theoretical sulfur content.   These pure samples of *p-tert*-amylphenol monosulfide were compounded as primary vulcanizing agents in a GR-S compound.   Stocks containing up to 30 parts of vulcanizing agent were tested.   The greater the amount of vulcanizing agent employed, the faster the stock cured.   However, all of these stocks were too slow curing for practical purposes, and the original stress-strain properties, even for a stock cured 240 minutes at 280° F, were quite inferior to the properties of stocks produced with elemental sulfur.

These results indicate that pure alkylphenol monosulfides, even when used in large quantities, are only mild vulcanizing agents for GR-S.   Data presented in this paper show that the disulfides apparently contain labile sulfur which is readily available for vulcanization, and, consequently, the disulfide serves as a much stronger primary vulcanizing agent.   The disulfides are prepared in excellent yields by a procedure similar to that outlined for the monosulfides, except that sulfur monochloride is substituted for the dichloride.   The stability of the alkylphenol sulfides in storage and under normal processing conditions is entirely satisfactory.   Samples of these sulfides which had been heated for as long as 168 hours at 125° C showed no visible change in physical properties. Furthermore, vulcanizates prepared from both the heat-treated and untreated sulfides possessed the same physical properties.

Up to the present time no standard method for measuring the important property of tackiness in rubber has been developed.   Although the usual method of observing the cohesive and adhesive strengths of the uncured stock for tack is rather crude, with experience a tackiness-producing material can be evaluated for its practical application.

Experiments showed that phenol sulfides with alkyl groups of four or more carbon atoms are soluble in GR-S and have greater tackiness-producing properties than do sulfides with smaller alkyl groups.   Cresylic acid sulfides and xylenol sulfides, which have limited compatibility with GR-S, produce an opaque synthetic when used in amounts greater than 5 parts per 100 of rubber; however, these sulfides are fairly active vulcanizing agents.

There is some difficulty in attempting to evaluate the tackiness-producing qualities of alkylphenol sulfides differing only in the configuration of the alkyl group.   A similar difficulty arises as regards the exact determination of the effect of the position of the alkyl group in the phenol molecule.   Experimental evidence strongly demonstrated that alkylphenol sulfides containing *p-tert-*

alkyl groups are superior tackifiers for butadiene-styrene copolymers. There was little observable difference between the tackiness producing qualities of the phenol sulfides having either one or two alkyl groups in the same phenol molecule. However, it follows that, on a weight basis, the sulfide from a dialkylphenol would be a less active vulcanizing agent than the corresponding sulfide produced from monoalkylphenol. All of these comparisons were made on the basis of an equivalent sulfur-alkylphenol ratio.

Generally speaking, by increasing only the sulfur content, the tackiness-producing property of the alkylphenol sulfide is lessened and the vulcanizing ability increased. The type of sulfur linkage—that is, mono-, di-, or poly-—must be considered carefully, inasmuch as the di- or polysulfide molecules of high sulfur content must be used sparingly to avoid overcure. Furthermore, the monosulfides are used for maximum tack, and, since they are weak vulcanizing agents, elemental sulfur should be added to the compound to obtain normal cure.

Figure 1 shows a schematic relation between the tackiness-producing qualities and vulcanizing powers of alkylphenol sulfides differing with respect to
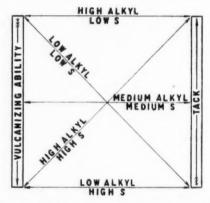
FIG. 1.—Schematic relation between tack qualities and vulcanizing powers of alkylphenol sulfides of various alkyl groups and sulfur content.

size of the alkyl groups and percentage of sulfur. A range of alkyl groups from one to ten carbon atoms has been considered as the limiting range for comparison. The sulfur content may vary over a wide range, from a trace of sulfur up to 40–50 per cent.

Naturally such a schematic diagram does not present a complete picture of all of the numerous variations that are possible with the alkylphenol sulfides. Figure 1 indicates that an alkylphenol sulfide possessing (1) a long alkyl group and high sulfur content imparts good tackiness and gives an overvulcanized compound; (2) a short alkyl group and low sulfur content give poor tackiness and an undervulcanized compound; (3) a long alkyl group and low sulfur content give good tackiness and an undervulcanized compound, (4) a short alkyl group and high sulfur content give poor tackiness and an overvulcanized compound, and (5) an alkyl group of medium chain length and medium sulfur content represents a compromise which would be the most practical from the standpoint of tackiness and vulcanizing power. Experimental evidence indicates that an alkylphenol disulfide having a C_4 to C_6 alkyl group with a sulfur

content ranging from 20 to 30 per cent produces optimum results in the buta-
diene copolymers. Buna-N polymers require a sulfide of somewhat higher
sulfur content than that needed for GR-S to produce normal vulcanizates.

Although alkylphenol sulfides function as tackifiers in GR-S, they are some-
what less effective for this purpose when used in Buna-N types. In addition
they are particularly effective in aiding in the retention of original tension
properties on aging, as they are in the case of GR-S.

As primary vulcanizing agents, alkylphenol sulfides cause blistering in
Butyl rubber (GR-I) stocks. However, preliminary results reveal that a
combination of alkylphenol sulfide and elemental sulfur can be employed to
produce GR-I vulcanizates of superior aging properties.

Based on laboratory tests conducted so far, alkylphenol sulfides appear to
function in the Neoprenes as accelerators.   On the other hand, several attempts
to utilize either mono- or disulfides as primary accelerators for natural rubber
or butadiene copolymers were unsuccessful. A limited examination of these
materials as vulcanizing agents in natural rubber, natural-rubber reclaim,
blends of natural rubber and natural-rubber reclaim, blends of natural rubber
with GR-S, and blends of natural-rubber reclaim and GR-S showed that the re-
sulting vulcanizates possess improved aging properties.

VARIATION OF ALKYL GROUPS

For the investigation of the effect of changes in the alkyl groups of this
series of compounds, a base recipe of the following composition was selected:

GR-S	100
Coal tar softener	5
Zinc oxide	5
EPC black	50
Mercaptobenzothiazole	1.6
Diphenylguanidine	0.1
Vulcanizing agent	Varies

In processing these stocks, the milling, curing, and testing procedures sug-
gested in the September 1, 1942, release from the office of the Rubber Director
of the War Production Board were followed, with only slight changes.   A
large master batch containing all the compounding ingredients except the vul-
canizing agent was prepared, split, and used for testing. All stocks after the
addition of the vulcanizing agent were allowed to rest 24 hours, refined by
two passes through a tight mill, and sheeted to the desired thickness before
curing.

The following physical testing procedures were employed in all of this work:

STRESS-STRAIN measurements were made by the A.S.T.M. procedure
as given in the A.S.T.M. Standards on Rubber Products D412–41 (1944).
Specimens measured at 212° F were preheated 30 minutes at this temperature
before testing.   The oven method of accelerated aging, D573–42, was followed,
using an operating temperature of 212° F for 72 hours.

TEAR RESISTANCE was determined by the A.S.T.M. procedure D624–41 T,
using Die B specimen.

PERMANENT SET was measured according to A.S.T.M. designation D412–41,
employing a T-50 specimen, which was stretched to 50 per cent of the ultimate
elongation (determined from stress-strain data) for 30 minutes. The final
reading was taken 10 minutes after release of tension.

COMPRESSION SET was determined by the A.S.T.M. procedure D395–40 T, method B, using a standard test-specimen molded to the required size.

DUROMETER HARDNESS was measured according to A.S.T.M. designation D676–42 T on tensile slab-specimens piled three high. All readings were instantaneous.

REBOUND measurements were made on the Lüpke Resiliometer on a cylindrical disk 1.129 inches in diameter and 0.5 inch in thickness.

HYSTERESIS was determined by the Goodrich Flexometer (in the V. L. Smithers laboratories) on pellets 0.7 inch in diameter cut from cylindrical disks 1.129 inch in diameter and 0.5 inch in thickness and stacked two high. The stroke was 0.175 inch and the load, 143 pounds per square inch. Specimens were preheated one hour at 212° F before flexing.

FLEX-CRACK GROWTH was measured on a T-50 specimen nicked on one side to a depth of 0.002 inch. The test conditions employed were 200 ± 50 per cent elongation at 375 cycles per minute. The flexing machine and the method employed were similar to those employed in the Columbia Carbon Company research laboratories, as described in their "Carbon Reinforcement of Buna-S", Volume IV, pages 123–5.

Table I shows the effect on physical properties of four different alkylphenol mono- and disulfides. The tackiness of the uncured stocks are also included for comparison. The same relative efficiency as that of tackifiers was found to hold when these alkylphenol sulfides were added to a GR-S gum stock in the amount of 10 parts per 100 of polymer.

Inasmuch as monosulfides are slower vulcanizing agents than disulfides when compared on an equivalent total sulfur basis, 0.8 part of elemental sulfur was added to the monosulfide stocks. Preliminary compounding data indicated that the monosulfides compounded with additional elemental sulfur in this manner produced vulcanizates approaching those stocks vulcanized with the corresponding disulfide without additional sulfur. The disulfides are as effective as elemental sulfur in the vulcanization of GR-S.

The sulfur content of each alkylphenol sulfide and the parts of each monosulfide and disulfide used per 100 parts of GR-S are listed in Table I. The disulfides are more active vulcanizing agents than the combination of monosulfides and sulfur. The results indicate that different alkyl groups do not produce widely divergent values for the physical properties studied. Cresol sulfides are the least active of the groups studied and have the disadvantage of being only fair tackifiers compared to other members of the series. All the alkylphenol disulfides investigated produce vulcanizates having stress-strain properties superior to the sulfur control. The retention of all tension properties after aging is noteworthy in all the alkylphenol sulfide stocks.

p-tert-AMYLPHENOL SULFIDES OF VARIOUS SULFUR CONTENT

The sulfides of p-tert-amylphenol derived from a commercially available phenol were chosen for this investigation and subsequent studies. The conclusions drawn from the discussion of Figure 1 governed this choice. Furthermore, these particular sulfides are readily soluble in GR-S and materially aid in the dispersion of the pigments.

Both p-tert-amylphenol monosulfide and the corresponding disulfide in three variations of sulfur content were investigated in a typical GR-S carbon black stock.

TABLE I
EFFECT OF VARIATION IN ALKYL GROUP OF ALKYL PHENOL SULFIDE ON PHYSICAL PROPERTIES IMPARTED TO GR-S VULCANIZATES

Alkyl group	Sulfur	Parts added per 100 rubber	Parts elemental sulfur added	Total sulfur	Tackiness of uncured stock	Cure at 280° F (min.)	Modulus at 300% (lbs. per sq. in.)	Tensile strength (lbs. per sq. in.)	Elongation (%)	Modulus at 300% (lbs. per sq. in.)	Tensile strength (lbs. per sq. in.)	Elongation (%)
							Original properties			**Aged properties***		
ALKYLPHENOL MONOSULFIDES												
Methyl (cresol)	18.3	8.75	0.8	2.4	Fair	60	410	1770	920	1150	2360	610
						90	610	2410	840	1350	2400	550
p-tert-Butyl	13.0	12.3	0.8	2.4	Good	60	430	1740	820	1130	2190	570
						90	630	2190	750	1350	2190	470
p-tert-Amyl	12.8	12.5	0.8	2.4	Good	60	510	1800	800	1130	2220	570
						90	700	2180	720	1350	2300	500
p-tert-Octyl	10.1	15.8	0.8	2.4	Good	60	480	2060	810	1320	2410	550
						90	670	2320	730	1410	2410	530
Elemental sulfur	..	..	2.4	2.4	Poor	60	660	2400	680	..	1690	190
						90	1320	2650	500	..	1700	160
ALKYLPHENOL DISULFIDES												
Methyl (cresol)	31.0	5.15	0	1.6	Fair	60	670	2100	760	1560	2590	500
						90	810	2390	710	1560	2670	510
p-tert-Butyl	23.3	6.9	0	1.6	Good	60	1020	2780	670	1900	2710	420
						90	1190	3040	640	1950	2750	410
p-tert-Amyl	23.0	7.0	0	1.6	Good	60	930	2910	730	1810	2810	460
						90	1130	2950	640	1820	2810	460
p-tert-Octyl	19.7	8.1	0	1.6	Good	60	1010	2890	680	1990	2860	430
						90	1210	3070	630	2010	2830	420
Elemental sulfur	..	..	1.6	1.6	Poor	60	340	1530	720	1760	2100	310
						90	810	2490	640	..	2210	280

* After aging 72 hours at 212° F in air oven.

The following table lists the sulfur content of these sulfides and the parts of vulcanizing agent added per 100 parts of GR-S:

Monosulfide			Monosulfide + sulfur			Disulfide		
Sulfur in sulfide (%)	Parts sulfide added	Total sulfur present	Parts sulfide added	Parts sulfur added	Total sulfur present	Sulfur in sulfide (%)	Parts sulfide added	Total sulfur present
9.0	17.9	1.6	17.9 + 1.6		3.2	16.4	9.7	1.6
12.8	12.5	1.6	12.5 + 1.6		3.2	23.0	7.0	1.6
16.5	9.7	1.6	9.7 + 1.6		3.2	28.0	5.6	1.6
Sulfur control	..	1.6	..	..	..	..	..	1.6

The formula employed was:

GR-S	100.0
Coal tar softener	4.5
Stearic acid	1.0
Zinc oxide	3.0
EPC black	43.0
Mercaptobenzothiazole	1.6
Diphenylguanidine	0.1
Vulcanizing agent	Variable

Cures were 20, 45, 60, and 90 minutes at 280° F.

Since the purpose of this phase of the investigation was to determine the effect of varying sulfur content in p-tert-amylphenol sulfide on the rate of curing, these sulfides were compounded on the basis of equivalent sulfur. The monosulfides were compounded both as a primary vulcanizing agent and as covulcanizing agents with elemental sulfur.
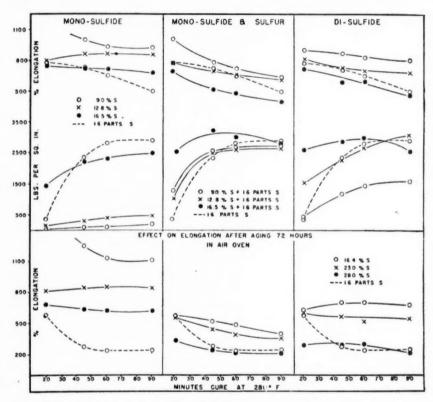
Figure 2 compares p-tert-amylphenol sulfides and elemental sulfur with respect to the tensile strength and elongation imparted to a GR-S tread-type stock. The monosulfide stocks containing no elemental sulfur are definitely slower curing than the stocks vulcanized with sulfur. This fact is clearly shown in Figure 2 by the high elongation values even after aging for three days at an elevated temperature. However, stocks containing both a monosulfide and elemental sulfur are all faster curing than the control vulcanized with elemental sulfur alone. Figure 2 also shows the detrimental effect of this additional sulfur by the sharp drop in elongation after aging.

The disulfide vulcanizates present a somewhat different picture. The p-tert-amylphenol disulfide of 16.4 per cent sulfur content produces slower curing stocks than does elemental sulfur. The p-tert-amylphenol disulfide of 28 per cent sulfur content, on the other hand, is a rapid vulcanizing agent for GR-S, and the vulcanizates produced are comparable in elongation with those obtained with sulfur. Of the three p-tert-amylphenol disulfides of varying sulfur content, the one of 23 per cent sulfur content appears to be the most advantageous from the standpoint of the quality of the vulcanizates produced. GR-S vulcanizates produced with this particular alkylphenol disulfide have the advantage of high tensile strength, high elongation, and unusual resistance to aging. Additional advantages of this vulcanizing agent are shown in Table II.

p-tert-AMYLPHENOL DISULFIDE (23 PER CENT SULFUR) IN VARYING AMOUNTS

At this point the effect of using different amounts of p-tert-amylphenol disulfide of 23 per cent sulfur content seemed to warrant investigation. Vulcanizates having four different total sulfur contents were studied. The formula

employed was the same as that used in the preceding series, except that in the case of the elemental sulfur stocks, 2.0 parts of a rosin-type softener were added.   The alkylphenol sulfides were checked also for their tackiness-producing qualities, and this rosin type of softener was added to the elemental sulfur stocks for comparative purposes.   Figure 3 shows the effect on stress-strain properties of varying amounts of vulcanizing agent before and after aging 72 hours in an air oven at 212° F.   With one exception the *p-tert*-amylphenol disulfide vulcanizates are superior in tensile strength and elongation

FIG. 2.—Tensile strength and elongation *vs.* time of cure for *p-tert*-amylphenol sulfide vulcanizates of varying sulfur content.

to the corresponding elemental sulfur vulcanizates.   The elongation values of the 1.0-part elemental sulfur stock after aging are due to the fact that the original stock was undercured to a greater extent than was the corresponding sulfide stock.   The tensile data clearly indicate that *p-tert*-amylphenol disulfide of 23 per cent sulfur content produces a faster rate of curing in GR-S than does an equivalent amount of elemental sulfur.

EPC, FT, AND SRF CARBON BLACKS

The proper type and amount of carbon black are important considerations in the reinforcement of GR-S.   Garvey and Freese[7] investigated ten types of

TABLE II

TEAR RESISTANCE AND FLEX-CRACK GROWTH OF GR-S STOCKS
REINFORCED WITH VARIOUS AMOUNTS OF EPC, FT, OR SRF
BLACK AND VULCANIZED WITH p-tert-AMYLPHENOL
DISULFIDE OR SULFUR

Parts carbon black	Minutes to optimum cure at (280° F)	p-tert-Amylphenol disulfide			Sulfur		
		Tear resistance lbs. per sq. in.		Flex-crack growth (cycles to failure)	Tear resistance lbs. per sq. in.		Flex-crack growth (cycles to failure)
		Original	212° F		Original	212° F	
EPC Black							
20	60	133	50	2,360	100	26	4,750
40	75	412	203	6,400	383	177	4,800
50	75	527	500	16,250	412	254	3,560
75	90	528	313	Broke	386	243	3,180
100	90	356	185	Broke	314	153	187
FT Black							
20	45	77	20	1,500	29	17	25
30	45	93	26	3,280	40	17	75
40	45	164	41	10,980	85	21	375
50	45	191	96	18,600	131	28	1,182
75	30	224	135	40,500	160	97	3,182
100	30	237	133	60,000	215	138	14,500
SRF Black							
20	45	143	30	3,560	45	19	288
40	45	228	57	9,300	113	32	189
50	45	403	205	55,875	170	70	281
75	45	350	270	4,870	220	92	175
100	30	356	135	Broke	274	76	Broke
150	30	268	79	Broke	215	68	Broke

carbon blacks in various loadings in GR-S using sulfur vulcanization. Inasmuch as the previous work indicated that alkylphenol sulfides improved vulcanizates containing 40–50 parts of EPC (easy processing channel) black, this investigation was extended to other loadings. FT (fine thermal) and SRF (semireinforcing furnace) blacks were also included in the series. p-tert-Amylphenol disulfide of 23 per cent sulfur content was used throughout. The formula employed was the first one listed in the section of this paper on variation of alkyl groups. Cures were 30, 60, 90, 120, and 180 minutes at 280° F. Data on the curves for tensile strength and elongation against loading were selected from the considered optimum cure of each black loading. These properties were evaluated at room temperature, at 212° F, and after accelerated air oven aging for 72 hours at 212° F.

FPC Black.—Figure 4 shows the effect of different loadings of EPC black on the tensile strength of GR-S when vulcanized with p-tert-amylphenol disulfide or sulfur. In the lower range of loadings the sulfide vulcanizates demonstrate a more pronounced improvement over sulfur. For the entire range of loadings the p-tert-amylphenol disulfide imparts improved tensile strength, particularly in the case of the unaged stocks. Figure 4 gives corresponding data for elongation. Retention of elongation after aging is particularly noteworthy for the sulfide vulcanizates at the lower loadings.

FT Black.—Vulcanization with p-tert-amylphenol disulfide of GR-S reinforced with FT black shows greater improvement over vulcanization with elemental sulfur than when either of the other types of carbon black studied
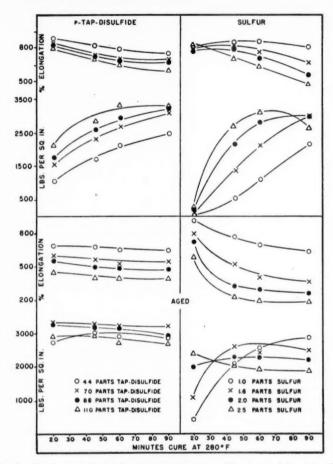
Fig. 3.—Tensile strength and elongation *vs.* time of cure for *p-tert*-amylphenol disulfide and sulfur vulcanizates. *p*-TAP-disulfide = *p-tert*-amylphenol disulfide.

is employed. FT black, one of the coarser particle size blacks, is a rather poor reinforcing agent for GR-S when normal sulfur vulcanization is employed. However, the data shown in Figure 5 demonstrate that tensile strength and elongation can be enhanced considerably in the case of FT black by the use of *p-tert*-amylphenol disulfide. The marked rise in elongation with increased carbon black loading, for the sulfide vulcanizates at 212° F and for the sulfur vucanizates at room tmperature, is peculiar to this type of black.

SRF Black.—*p-tert*-Amylphenol disulfide is superior to sulfur as a vulcanizing agent for improving the tensile strength and elongation of GR-S stocks reinforced with SRF black in the range of loadings up to 75 parts black per 100 of rubber. Here again the retention of elongation at 212° F and after hot-air aging is noteworthy for the sulfide vulcanizates. These data are illustrated in Figure 6.

It is generally accepted that low modulus and high elongations are accompanied by good resistance to flex-crack growth. Thus undercures resist flex-
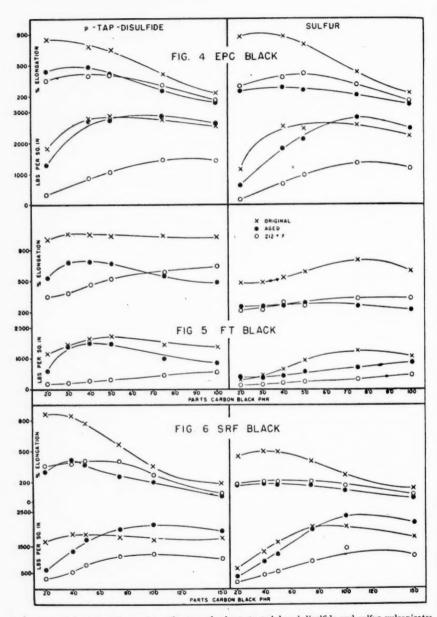
FIGS. 4, 5, and 6.—Elongation and tensile strength of *p-tert*-amylphenol disulfide and sulfur vulcanizates for various carbon black loadings.

crack growth better than normal- or overcures. It follows that any method of compounding or curing which aids in the retention of the original tensile properties after aging also improves resistance to flex-crack growth. The data shown in Figures 4, 5, and 6 clearly illustrate the improved aging properties of p-tert-amylphenol disulfide vulcanizates as compared to the corresponding sulfur vulcanizates. The influence of vulcanization with the alkylphenol sulfides on tear resistance and flex-crack growth was investigated with a series of stocks involving all three types of blacks. In every case the use of p-tert-amylphenol disulfide resulted in a marked improvement in these physical properties. These values are shown in Table II along with the optimum cure times chosen for comparison of the properties of tensile strength and elongation over the range of different carbon black loadings.

REPRESENTATIVE TREAD STOCK

For comparison of p-tert-amylphenol disulfide and sulfur in a typical GR-S tread stock, the following formulations were studied:

Stock	A	B	C	D
GR-S	100	100	100	100
EPC black	45	45	45	45
Coal tar softener	4	4	4	4
Pine tar	..	3	..	3
Stearic acid	2.5	2.5	2.5	2.5
Zinc oxide	2.5	2.5	2.5	2.5
N-Cyclohexyl-2-benzothiazole sulfenamide	1.2	1.2	1.2	1.2
Phenyl-β-naphthylamine	0.6	0.6	0.6	0.6
Cupric diethyldithiocarbamate	..	..	0.1	0.1
p-tert-Amylphenol disulfide (23% S)	8.0	..	8.0	..
Sulfur	..	1.7	..	1.7
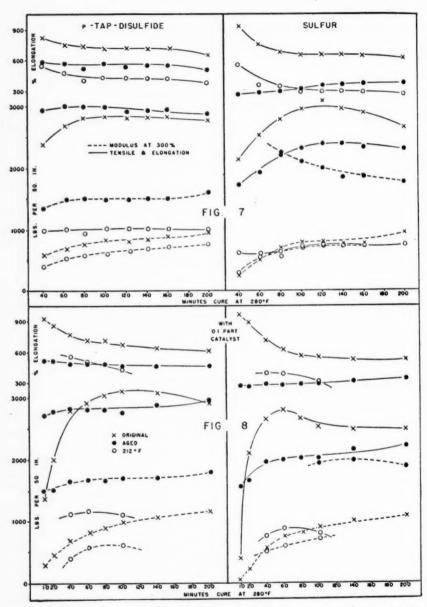
Cures were 20, 40, 60, 80, 100, 120, 140, 160, and 200 minutes at 280° F.

The formula selected in this case is not radically different from those used in the previous work. The accelerator was changed to a derivative of mercaptobenzothiazole, N-cyclohexyl-2-benzothiazole sulfenamide, and, in the case of the stocks cured with elemental sulfur, 3.0 parts of pine tar were added. In the case of the stock vulcanized with p-tert-amylphenol disulfide, this softener showed a slight retarding effect and therefore was omitted.

The use of copper compounds as boosters for mercaptobenzothiazole type accelerators was discussed by Somerville[8]. Stocks C and D are, respectively, the p-tert-amylphenol disulfide and sulfur vulcanizates containing 0.1 part of cupric diethyldithiocarbamate added for this purpose. Examination of the stress-strain data shown in Figures 7 and 8 shows that the curing time is reduced approximately one fourth by the use of this co-accelerator.

Some of the more common physical properties which are pertinent to a tread stock are given in Figures 7 and 8 and Table III. Modulus values at 300 per cent under normal conditions, at 212° F, and after aging in an air oven 72 hours at 212° F, are shown in these figures. The stocks vulcanized with p-tert-amylphenol disulfide exhibited a smaller change in modulus after aging and at 212° F than did the corresponding stocks vulcanized with sulfur. The sulfur vulcanizates, on the other hand, demonstrated the well known fact that undercures age poorly, whereas overcures age well, all considerations being made on a percentage basis. This is not true for the corresponding disulfide vulcanizates.

FIGS. 7 and 8.—Elongation, tensile strength, and modulus at 300 per cent *vs.* time of cure in a tread stock, with and without 0.1 part catalyst.

TABLE III

PHYSICAL PROPERTIES OF A TYPICAL GR-S TREAD STOCK VULCANIZED WITH p-tert-AMYLPHENOL DISULFIDE OR WITH SULFUR

Stock	Cure at 280° F (min.)	Shore durometer hardness		Tear resistance (lbs. per sq. in.)			Flex-crack growth, cycles to failure			Heat build-up temp. rise above 212° F original	Rebound (%)		Compression set on original (%)	Permanent set on original (%)
		Original	Aged*	Original	Aged*	212° F	Original	Aged*	212° F		Original	212° F		
A	60	66	70	535	435	253	44,400	14,100	30,300	···	46	51	59	19
	100	66	74	547	449	238	22,725	12,750	1,780	···	47	54	47	14
	120	66	74	···	···	···	···	···	···	306	···	···	···	···
	160	65	70	553	514	250	19,425	5,460	750	298	47	54	44	14
B	60	55	70	394	227	182	19,000	Broke	18,000	···	45	53	47	12
	100	61	72	392	231	195	6,250	Broke	281	263	47	57	29	8
	120	62	71	···	···	···	···	···	···	257	···	···	···	···
	160	60	70	360	258	176	3,940	Broke	Broke	···†	48	60	22	8
C	40	65	72	640	371	253	15,750	Broke	15,000	···	46	50	57	17
	60	65	73	587	353	262	5,800	Broke	7,935	312	47	53	50	15
	100	67	71	419	283	255	4,590	Broke	1,970	306	47	53	42	13
	120	···	···	···	···	···	···	···	···	···	···	···	···	···
D	40	60	71	390	175	183	6,680	Broke	Broke	···	47	56	34	10
	60	60	70	353	182	180	3,000	Broke	Broke	···	49	59	26	8
	100	65	70	330	179	150	875	Broke	Broke	254	49	61	21	8
	120	···	···	···	···	···	···	···	···	···	···	···	···	···

* Aged 72 hours at 212° F in air oven.
† Specimen slipped out of machine.

Tensile strength and modulus values determined under the same conditions are plotted in the same figures. The most striking observation is that, although the tensile strength values of the four stocks are quite comparable for the unaged materials, after aging the tensile strength of the disulfide vulcanizates showed very little change whereas those of the sulfur vulcanizate dropped appreciably. Tensile strength at 212° F was also greater for the *p-tert*-amylphenol disulfide vulcanizates. Retention of elongation at 212° F and after aging in the case of *p-tert*-amylphenol disulfide in contrast to sulfur is portrayed in Figures 7 and 8.

Rather close harmony of the Shore hardness values of these types of vulcanizates is shown in Table III. Although *p-tert*-amylphenol disulfide produced somewhat higher initial hardness values than does sulfur, the percentage increase in hardness after aging was not so great. Tear resistance and flex-crack growth at room temperature, 212° F, and after air oven aging for 72 hours at 212° F are shown also in Table III. *p-tert*-Amylphenol disulfide imparted greatly improved tear resistance and flex-crack growth to the tread stock. Although the presence of cupric diethyldithiocarbamate improved the tear resistance of the amylphenol disulfide vulcanizate, the resistance to flex-crack growth was decreased due to the higher state of cure. Under the conditions of testing, several of the specimens broke at the start of the flex-crack growth test.

These improvements in resistance to tear and flex-crack growth are accompanied by an increase in hysteresis, as shown by the higher heat build-up values listed for stocks A and C. Some sacrifice in rebound resilience, compression set, and permanent set resulted from the use of *p-tert*-amylphenol disulfide. However, improvement in these physical properties was made by the use of the copper co-accelerator, as shown in stock C. These shortcomings also can be compensated for, to some degree, by the addition of softeners and plasticizers.

MINERAL FILLERS

Preliminary work showed that amylphenol disulfides may be adapted for the vulcanization of GR-S stocks loaded with the mineral fillers to produce improved physical properties similar to those shown by the carbon black stocks. Five mineral fillers were compounded in a GR-S stock on a basis of 40 parts by volume.

Typical properties conferred by *p-tert*-amylphenol disulfide with the various mineral fillers are illustrated by the series of stocks in Table IV.

All of the stocks containing mineral fillers were greatly improved in modulus, tensile strength, elongation, and tear resistance through vulcanization with *p-tert*-amylphenol disulfide.

Later work showed that much greater improvements in stress-strain properties can be obtained by the use of mineral fillers of much finer particle size. The optimum cures selected for each mineral filler were the same for both types of vulcanizates. These cures were chosen from modulus–time of cure curves, with the selected curing time that point at which the cure began to have a constant slope.

After a long curing time, stocks reinforced with hard clay possessed the highest tensile strength for both types of vulcanizing agents. In these same clay stocks sulfur produced slightly higher elongation than *p-tert*-amylphenol disulfide, but this superiority was not manifested after aging. The stock reinforced with hydrated alumina was considerably improved in tensile strength

TABLE IV

Physical Properties of GR-S Stocks Loaded with Various Mineral Fillers and Vulcanized with p-tert-Amylphenol Disulfide or Sulfur

Compound	E	F	G	H	I	J	K	L	M	N
GR-S	100	100	100	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2
Tetraethylthiuram disulfide	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35
Butyraldehyde-aniline	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
p-tert-Amylphenol disulfide (23% S)	10.5	10.5	10.5	10.5	10.5					
Sulfur						2.25	2.25	2.25	2.25	2.25
Pptd. calcium carbonate	115					115				
Hard clay		110.8					110.8			
Titanium dioxide			166					166		
Hydrated alumina				103.5					103.5	
Basic magnesium carbonate					94.25					94.25
				Original properties						
Optimum cure at 280° F (min.)	45	90	45	30	45	45	90	45	30	45
Modulus at 300% (lbs. per sq. in.)	210	390	230	160	240	210	340	270	460	390
Tensile strength (lbs. per sq. in.)	1000	1510	1000	1310	910	600	1270	700	650	570
Elongation (%)	810	760	660	940	770	480	820	440	350	350
Shore hardness	70	70	74	66	70	65	62	69	65	65
Tear resistance (lbs. per in.)	91	150.5	140	184.5	165	89	136	88	78	85
				After aging 72 hours in air oven at 212° F						
Modulus at 300% (lbs. per sq. in.)	270	550	350	270	270	290	690	410	580	530
Tensile strength (lbs. per sq. in.)	840	1670	930	1220	1000	520	1100	610	580	600
Elongation (%)	600	620	490	600	580	390	570	350	300	340
Shore hardness	74	76	75	75	70	65	71	74	71	74

and elongation by the use of this alkylphenol sulfide, and required the shortest time to reach optimum cure. The other three mineral fillers—precipitated calcium carbonate, titanium dioxide, and basic magnesium carbonate—produced comparable stress-strain data; although they were inferior to the first two mineral fillers discussed, p-tert-amylphenol disulfide offered an improvement over sulfur. A marked decrease in elongation after aging was not exhibited in the case of the GR-S stocks containing mineral fillers and vulcanized with sulfur, as in the case of the carbon blacks. The tear resistance of all the vulcanizates cured with p-tert-amylphenol disulfide was superior to that of sulfur-cured GR-S.

p-tert-AMYLPHENOL DISULFIDE IN BUNA N

The results of a preliminary investigation indicated that p-tert-amylphenol disulfide of 28 per cent sulfur content is more adaptable than the 23 per cent sulfur compound when used with Buna-N copolymers. Typical properties imparted by the disulfide are illustrated by the following series of stocks:

Stock	O	P	Q	R
Buna-N (high acrylonitrile content)	100	100	100	100
Zinc oxide	5	5	5	5
Stearic acid	0.5	0.5	0.5	0.5
MPC black	50	50	50	50
Benzothiazyl disulfide	1.5	1.5	..	..
Tetraethylthiuram disulfide	..	..	0.4	0.4
p-tert-Amylphenol disulfide (28% S)	5.5	..	5.5	..
Sulfur	..	1.5	..	1.5

Cures were 5, 10, 20, 30, 45, 60, 75, and 90 minutes at 310° F.

The values of tensile strength, modulus at 300 per cent, elongation, and hardness of the vulcanizates obtained with p-tert-amylphenol disulfide or sulfur are listed in Table V. The disulfide imparted lower modulus, higher tensile strength, and higher elongation to the Buna-N vulcanizate both before and after air-oven aging for 72 hours at 212° F. When the disulfide was used in this amount, it was a slower vulcanizing agent than sulfur. The rate of cure

TABLE V

PHYSICAL PROPERTIES OF BUNA N VULCANIZATES

Stock	Cure at 310° F (min.)	Modulus at 300% (lbs. per sq. in.)		Tensile strength (lbs. per sq. in.)		Elongation (%)		Shore hardness	
		Original	Aged*	Original	Aged*	Original	Aged*	Original	Aged*
O	20	850	2390	1890	3300	770	400	75	80
	45	1790	3190	3410	3730	520	350	77	80
	75	2420	4000	4280	4390	460	320	80	84
P	20	2430	..	3790	3520	430	210	76	80
	30	3000	..	3850	3200	370	210	79	80
	45	3330	..	3880	3200	340	210	79	80
Q	10	610	2790	1510	4330	820	450	70	79
	45	1610	3700	3870	3920	600	320	75	80
	75	1990	3900	4270	4190	530	310	75	81
R	5	1140	..	2750	3240	640	180	70	80
	10	2420	..	3870	2670	410	180	73	81
	45	..	..	2900	3000	250	180	75	81

* Aged 72 hours at 212° F in an air oven.

can be increased to some extent by the use of a thiuram type of accelerator (stock Q) in place of the more conventional mercaptobenzothiazole type of accelerator (stock O).

CONCLUSIONS

An approach to the problem of improving the property of tackiness of butadiene copolymers and a new class of vulcanizing agents for these polymers are discussed. The tack-producing qualities of a number of the alkylphenol sulfides were investigated with respect to their molecular structure and sulfur content. The precise adjustment of the state of vulcanization is fundamental to the problem of improving the quality of vulcanizates of the butadiene co-polymers. The principal approach to the realization of this adjustment previously has been by means of acceleration. It has since been found that the choice of the proper type of vulcanizing agent offers an equally promising approach whereby improvements in quality of the product may be achieved.

ACKNOWLEDGMENT

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DEVELOPMENT OF A BETTER
PROCESSING GR-S*

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Poor processability has long been recognized as one of the shortcomings of GR-S. Since the problem is of major importance, this deficiency has been the subject of a number of investigations. Freshly milled samples of GR-S shrink rapidly and become very rough. Samples extruded through a die swell excessively and give irregular and broken edges. These faults have, in many instances, necessitated excessive loading with compounding materials to permit satisfactory calendering and extrusion. Sacrifices in quality have often been tolerated to obtain suitable processing. The present paper describes a new type of GR-S in which vastly improved processing properties have been imparted to the polymer during the copolymerization reaction.

PLASTICIZATION

An earlier report[1] on the plasticization of GR-S revealed that breakdown of the raw polymer on a hot mill gave a subsequent compound which tubed more smoothly and exhibited less swelling at the die. It was observed also that hot plasticization reduced the Mooney viscosity but at the same time decreased the solubility of the polymer in benzene. These effects were attributed to the formation of a cross-linked structure (gel phase), accompanied by chain scission. Table I gives data extracted from the report showing these relations[1], and

TABLE I
IMPROVED PROCESSING BY HOT MILLING[1]

Minutes on hot mill	Unmilled	20	40
Mooney viscosity	62	30	24
Percentage gel	0.3	37.1	44.8
Percentage swell at die*	51.6	35.6	3.07
Surface appearance	Rough	Smooth	Very smooth

* Calculated as increase in diameter from the original data which were reported as increase in area.

Figure 1 pictures the correlation of swelling at die and gel content with time of hot milling. Two other reports[2] extended this concept to show a positive correlation between gel content and processability of GR-S. They also review much of the available literature on this subject.

The methods for measuring processability have already been published[3]. The processing tests used as criteria in the present work include the determination of shrinkage and rugosity of calendered samples and tubing characteristics on extrusion through a Garvey die[4]. Shrinkage is determined by measuring the final length of samples which had previously been marked at definite inter-

vals on a constant-temperature free-running calender roll; it is expressed as a percentage of the original length.   Rugosity or roughness is determined on the same calendered samples, following the published procedure[5].   It is a measure of the average hill height and is determined by the rate of air passage between the sample and a flat disk.   Extrudability is rated by the swelling at the die, tubing rate, and surface appearance of extruded samples.
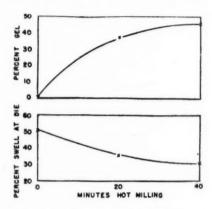
Fig. 1.—Improved processing by hot milling.

LATEX BLENDING

Concurrent with the improvement in processing obtained with hot-milled polymers was a corresponding sacrifice in some physical properties.   Moreover, the hot plasticization technique was time-consuming and expensive.   These facts led to the attempt to duplicate and surpass the effects of plasticization by exercising greater control over molecular structure of the polymer during polymerization.   This goal was attained in part by blending latices of different molecular characteristics.   One component of the blend was a polymer of very high Mooney viscosity and high gel content.   The other component was gel-free and of very low viscosity.   The resulting latex blend yielded a polymer self-plasticized by the low-molecular-weight component, yet containing the gel fraction necessary for low shrinkage.   As expected, its molecular-weight distribution was extremely broad.

The processing properties of the polymer derived from this latex blend agreed well with theory.   As Figure 2 shows, calender shrinkage was reduced from 46 per cent for standard GR-S to 33 per cent for the blend.   Calender rugosity was decreased from 0.15 to 0.10 unit.   Swelling at the extrusion die was reduced from 50 to 36 per cent.   The gel content of the blend was 39 per cent, the standard was gel-free.   Figure 3 shows how tubing is improved with a blend as compared to unplasticized and to hot-plasticized GR-S.   It is apparent that the blend with its low swell maintained more clearly the image of the Garvey die and exhibited a smoother tubed surface.   Physical properties of the blend were generally comparable to those of the hot-plasticized GR-S.

CONTROLLED CROSS–LINKING

Although latex blending yielded a better processing polymer, it had the disadvantages of requiring the preparation, storage, and controlled blending of
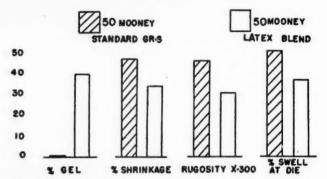
FIG. 2.—Improved processing from blending high and low Mooney latices.

different latices.   Accordingly a means was sought to produce the same effects in a single-step process.   This was realized by the introduction into the polymerization formula of small amounts of a cross-linking agent to tie the growing polymer chains together into a network or gel.   Such a technique had already been applied to insolubilize resins[6], but the only reported work with dienes[7] utilized such high concentrations of cross-linking agent that the polymer was no longer rubberlike.

Divinylbenzene was chosen as the most efficient cross-linking agent, and results obtained far exceeded expectations in that ultimate improvement in shrinkage and rugosity was much greater than had been achieved by any other method.   As little as 0.5 part of cross-linking agent substantially eliminated
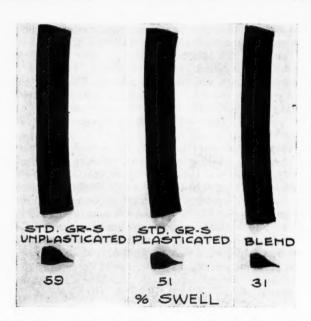
FIG. 3.—Improved tubing with GR-S made from high and low Mooney blends.

shrinkage, while calendered stocks remained almost as smooth as the calender rolls. Polymer prepared in accordance with this principle and containing 0.5 part divinylbenzene has been designated GR-S: X-285.

MILL BLENDS

Pictures of calendered and extruded samples of standard GR-S, X-285, and mill blends of the two in various proportions are shown in Figure 4, using the

GR-S 100 X-285 0	GR-S 75 X-285 25	-GR-S 50 X-285 50	GR-S 0 X-285 100

43 % SHRINKAGE   33 % SHRINKAGE   22 % SHRINKAGE   9% SHRINKAGE

0.15   0.09   0.05   0.02

ROUGHNESS

54%   42%   31%   15%

TUBING SWELLING

FIG. 4.—Improved processing with X-285 Type blends.

data of Table III. Comparison of the samples in Figure 4 shows that shrinkage is improved from 43 to 9 per cent, rugosity from 0.15 to 0.02 unit, and tubing swell from 54 to 15 per cent by substituting X-285 for standard GR-S. The mill blends of X-285 with standard GR-S give intermediate improvements. For a majority of uses such mill blends are to be preferred, since in this way the the altered physical properties of X-285 are less apparent and require less adjustment in compounding technique for any specific application.

Polymers prepared with lower concentrations of cross-linking agents were compared with mill blends of the more highly cross-linked variety. At equivalent processing levels the mill blends gave superior unaged tensile properties and cut growth resistance, as shown in Table II. Moreover, mill blending to

TABLE II

COMPARISON OF X-285 MILL BLEND AND A MODERATELY CROSS-LINKED POLYMER

Formula		
Standard GR-S	50	..
0.5 divinylbenzene polymer (X-285)	50	..
0.3 divinylbenzene polymer	..	100
EPC carbon black	50	· 50
Zinc oxide	5	5
BRT No. 7	5	5
Sulfur	2	2
Mercaptobenzothiazole	1.5	1.5
Mooney viscosity, compounded	77	74
Calender shrinkage (%)	22	27
Calender rugosity	0.05	0.07
Swell at die (%)	31	27
Tubing rate (grams per min.)	75	68
Properties of unaged compounds*		
Modulus at 300% (lb. per sq. in.)	900	550
Tensile (lb. per sq. in.)	2300	1720
Elongation (%)	550	620
Flex crack growth (mils per kilocycle)	3.4	5.6
Tensile of compounds* after aging 96 hrs. at 212° F (lb. per sq. in.)	1700	1800

* All cures at 292° F for 60 minutes.

the desired processability level permits both the compounder and the polymerization plant to keep a low inventory of one cross-linked polymer rather than a number of polymers of varying processability. It was for these reasons that the high cross-linked GR-S modification was selected for future development and has been produced as GR-S:X-285 for large scale experimentation by the rubber industry.

The slightly poorer unaged stress-strain properties of cross-linked stocks are balanced by a much better retentivity upon aging. Even without compounding adjustments, the cross-linked polymers become equal or superior to standard GR-S in tensile strength, modulus, and elongation after oven aging for 96 hours at 212° F. Figure 5 and Table III show these relations. Aged cut-growth data were too variable in this series to be significant and are not included. Indications are, however, that aging lessens the difference between the flexing properties of GR-S and X-285 blends.

COMPOUNDING ADJUSTMENTS

X-285 and its blends are appreciably altered in structure from standard GR-S, and compounding adjustments are required to secure the optimum properties for this type polymer.   The cross-linking reaction is similar to vulcanization in that both insolubilize the polymer.   This fact, coupled with the higher modulus throughout the curing range and the relation of low heat build-up to high cut growth shown in Figure 6, suggests that a reduction in sulfur is the most logical compounding variation, with or without an accelerator adjustment.
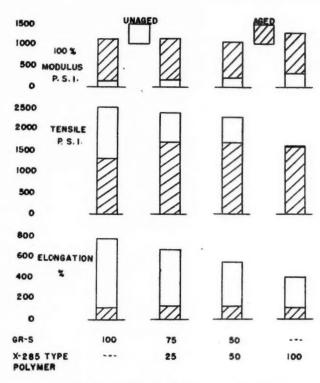
FIG. 5.—Aging of cross-linked mill blends, compounded with 2 parts sulfur and cured 60 minutes.

Figure 7 and Table IV compare the stress-strain properties of GR-S and a 50-50 blend of X-285 and GR-S at two sulfur levels in a typical carbon black recipe.   The lower sulfur level, 1.25 parts, gives the expected improvement in modulus and elongation at only a slight sacrifice in unaged tensile strength. After oven aging, however, the low sulfur blend becomes superior to standard GR-S.   Preliminary studies (not reported here) on X-285 blends with nonblack fillers indicate that a similar reduction in sulfur gives physical properties, unaged as well as aged, which are superior to standard GR-S compounded normally.   It is noteworthy that the processing improvements obtained with these nonblack loadings are fully equivalent to those prevailing in black compounds.

TABLE III

COMPARISON OF X-285 TYPE BLENDS WITH GR-S
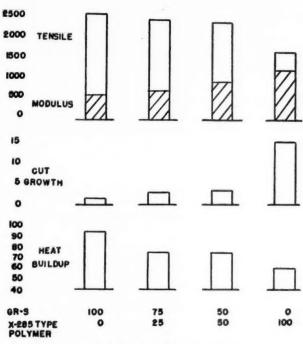
Formula				
Standard GR-S	100	75	50	..
X-285 type polymer	..	25	50	100
EPC carbon black	50	50	50	50
Zinc oxide	5	5	5	5
BRT No. 7	5	5	5	5
Sulfur	2	2	2	2
Mercaptobenzothiazole	1.5	1.5	1.5	1.5
Mooney viscosity				
After breakdown	30	30	29	29
Compounded	58	65	77	121
Calender shrinkage (%)	43	33	22	9
Calender rugosity	0.15	0.09	0.05	0.02
Swell at die (%)	54	42	31	15
Tubing rate (gram per min.)	69	70	75	54
Resilience after 60-min. cure				
Room temp.	37	37	36	36
212° F	45	48	48	52

Properties of unaged compounds (cured at 292° F)

Modulus at 300% (lb. per sq. in.)				
30-min. cure	200	200	390	600
60-min. cure	600	700	900	1190
90-min. cure	900	1000	1190	1500
Tensile (lb. per sq. in.)				
30-min. cure	1190	1190	1450	1000
60-min. cure	2520	2380	2300	1620
90-min. cure	2790	2300	2050	1700
Elongation (%)				
30-min. cure	875	820	700	465
60-min. cure	765	665	550	410
90-min. cure	635	505	465	355
Heat build-up in Goodrich flexometer (° F)				
30-min. cure	..	156	119	86
60-min. cure	94	75	76	61
90-min. cure	77	70	70	51
Av. flex crack growth				
(mils per kilocycle)	1.2	2.4	4.0	13.9

Properties of compounds after aging 96 hrs. at 212° F (cured at 292° F)

Modulus at 100% (lb. per sq. in.)				
30-min. cure	780	750	910	300
60-min. cure	1150	1150	1080	1290
90-min. cure	910	1150	1500	1400
Tensile (lb. per sq. in.)				
30-min. cure	1490	1400	1450	1300
60-min. cure	1310	1700	1700	1600
90-min. cure	1710	1150	1500	1400
Elongation (%)				
30-min. cure	150	150	140	100
60-min. cure	110	125	125	120
90-min. cure	150	100	125	100

In addition to sulfur and accelerator adjustments, the altered solubility characteristics of X-285 blends suggest that a study of different types of plasticizers might be beneficial. It is apparent also that the improved processability of X-285 blends will permit a reduction in filler and softener loadings

Fig. 6

TENSILE
2500
2000
1500
MODULUS
1000
500
0

CUT
GROWTH
15
10
5
0

HEAT
BUILDUP
100
90
80
70
60
50
40

| GR-S | 100 | 75 | 50 | 0 |
| X-285 TYPE POLYMER | 0 | 25 | 50 | 100 |

Fig. 6.—Comparative physical properties of cross-linked polymer mill blends, cured 60 minutes.

Fig. 7

UNAGED   AGED

100 %
MODULUS
P. S. I
1000
800
600
400
200
0

TENSILE
P. S. I.
3000
2000
1000
0

ELONGATION
%
800
600
400
200
0

SULFUR	2	2	1.25
GR-S	100	50	50
X-285 TYPE POLYMER	··	50	50
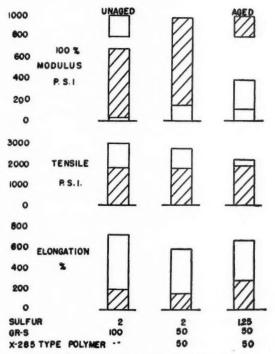
Fig. 7.—Effect of reduced sulfur on cross-linked blends.

TABLE IV

EFFECT OF REDUCED SULFUR ON AN X-285 TYPE BLEND.

Formula			
Standard GR-S	100	50	50
X-285 type polymer	..	50	50
EPC carbon black	50	50	50
Zinc oxide	5	5	5
BRT No. 7	5	5	5
Sulfur	2	2	1.25
Mercaptobenzothiazole	1.5	1.5	1.5
Mooney viscosity, compounded	54	89	82
Calender shrinkage (%)	47	28	26
Calender rugosity	0.15	0.10	0.10
Swelling at die (%)	53	31	28
Tubing rate (grams per min.)	74	68	71
Resilience at room temp. (60-min. cure)	40	38	37

Properties of unaged compounds (cured at 292° F)
Modulus at 300% (lb. per sq. in.)

30-min. cure	220	600	390
60-min. cure	680	1100	650
90-min. cure	1000	1410	900

Tensile (lb. per sq. in.)

30-min. cure	1600	1950	1190
60-min. cure	2950	2700	2150
90-min. cure	2990	2620	2500

Elongation (%)

30-min. cure	865	715	750
60-min. cure	720	585	660
90-min. cure	625	485	615

Av. flex crack growth (mils per kilocycle)	1.5	4.2	4.7

Properties of compounds after aging 96 hrs. at 212° F (cured at 292° F)
Modulus at 100% (lb. per sq. in.)

30-min. cure	700	1000	390
60-min. cure	680	980	390
90-min. cure	600	1020	450

Tensile (lb. per sq. in.)

30-min. cure	1400	1410	1950
60-min. cure	1800	1750	1850
90-min. cure	1750	1500	1990

Elongation (%)

30-min. cure	165	150	300
60-min. cure	200	160	290
90-min. cure	200	126	300

Av. flex crack growth (mils per kilocycle)	5.0	12.4	4.8

where these have been excessive heretofore to achieve tolerable processability. Such a reduction offers the possibility of an overall improvement in physical properties as well as processability.

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THIURAM DISULFIDES IN COMPOUNDING *

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Perhaps the chief drawback to the greater employment of thiuram disulfides has been the fear, often groundless, of scorching during processing, and for this reason the work detailed in this paper is devoted entirely to this aspect of their use. The scorching tendency, taken as the commencement of cure, and the rate of vulcanization were studied by means of a modified Goodrich type of plastometer, and the results are expressed as the percentage recovery against time in minutes at 120° C. This temperature (equivalent to 15 lbs. per sq. in. steam pressure) was chosen as being the highest likely to be reached in normal mixing, calendering and extrusion.

The rubber compounds tested were prepared from one large batch of base stock comprising: smoked sheet rubber, 100 parts; zinc oxide, 5 parts; and stearic acid, 2 parts.

After mixing, the stock was divided into the required number of portions and to these were added the various ingredients detailed later; in all cases the same milling time and temperatures were adhered to so that results would be comparable, especially plasticity. An interval of 24 hours at room temperature was allowed in each case before cutting plastometer test-pieces to dissipate strains imposed in the stock during mixing and sheeting. The test-pieces were then placed in an oven at 120° C, and percentage recovery determinations were made at 5-minute intervals over a range of 5 to 60 minutes.

Tetramethylthiuram disulfide (T.M.T.)—The properties of T.M.T. as a vulcanizing agent were then studied by preparing mixes containing 2 per cent, 3 per cent, and 4 per cent of T.M.T. The 2 per cent stock gave a recovery of 13 per cent up to 30 minutes, 17 per cent at 35 minutes, and rapidly increased thereafter to 46 per cent at 45 minutes, reaching a maximum of 87 per cent after 60 minutes; hence vulcanization commenced after 30 minutes and was complete at 60 minutes.

The 3 per cent stock commenced curing at 30 minutes and reached maximum recovery at 55 minutes.

In the case of the 4 per cent stock, vulcanization commenced after 20 minutes, and maximum recovery was reached in 45 minutes.

By this series it is shown that, using T.M.T. alone, the scorching tendency and rate of curing are greater with increased proportions of accelerator, but not in direct proportion to the increase of the latter.

Tetramethylthiuram disulfide and Sulfur.—The effect of varying percentages of T.M.T. used as a primary accelerator in stocks containing 1 per cent of sulfur was studied by incorporating 0.25 per cent, 0.5 per cent, and 0.75 per cent of T.M.T.

The 0.25 per cent mix had a recovery of 14 per cent up to 50 minutes, at which point curing commenced, and the recovery reached 20 per cent at 60

1.	T.M.T.	2%	Factice 30%	4. T.M.T.	2%	Nonox-S 2%
2.	T.M.T.	2%	Black 30%	5. T.M.T.	2%	Litharge 10%
3.	T.M.T.	2%	Clay 30%	6. Sulfur	0.3%	Litharge 10%
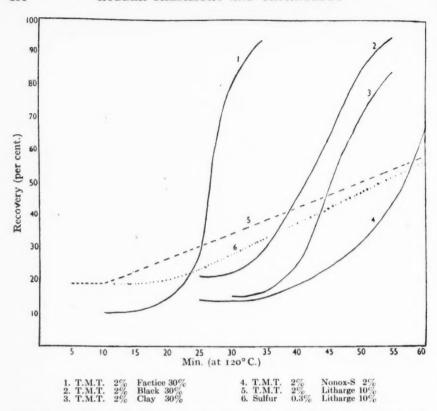
minutes. The 0.5 per cent mix set-up after 30 minutes, but the recovery only reached 38 per cent at 60 minutes, and the 0.75 per cent mix commenced curing in 30 minutes and reached maximum recovery in 60 minutes.

From this it is inferred that, with 1 per cent of sulfur, the minimum T.M.T. requirement for full vulcanization is about 0.75 per cent and the curing characteristics are then similar to a straight 2 per cent T.M.T. mix. Again it will be observed that the scorching tendency does not increase in direct proportion to increase of accelerator; in fact, the 0.5 and 0.75 per cent compounds appear to be similar in this respect.

Tetramethylthiuram disulfide and Litharge.—The effect of litharge on T.M.T. acceleration was investigated by incorporating 10 per cent litharge with 2 per cent T.M.T. In this case the onset of cure occurred in 10 minutes, and the progress of cure was directly proportional to time, *i.e.*, the graph of time against percentage recovery was a straight line. The rate of cure was about one-half that of a straight 2 per cent T.M.T. stock, although the set-up commenced 10 minutes sooner. From these results it is gathered that litharge considerably increases the scorching tendency of T.M.T., reducing scorching time by about 50 per cent, but slows the rate of curing to about one-half. To throw light on this interference, the scorch curve was repeated using 10 per cent of litharge, as before, but replacing the 2 per cent T.M.T. by 0.3 per cent of sulfur, which is the theoretical amount of sulfur obtainable from 2 per cent of T.M.T. It was found that the commencement of curing was delayed 100 per cent compared

with litharge-T.M.T., but that the rate of cure was slightly greater. An explanation of these results is difficult, but it would appear that, apart from an earlier start, litharge-T.M.T. acceleration is, in effect the same as litharge plus the equivalent amount of elementary sulfur. Stated otherwise, it seems that, of the break-down products of T.M.T. on cure, only the liberated sulfur is effective; the other products, monosulfide or dithiocarbamic acid, are "screened" or otherwise rendered ineffective by the litharge. It is appreciated that litharge is not generally employed in such high percentages, the object in doing so was to exaggerate its effect on the accelerator.

Tetramethylthiuram disulfide and Factice.—References in the literature indicate that brown factice has a retarding effect on T.M.T., but results obtained using 30 per cent of brown factice and 2 per cent of T.M.T. showed the opposite to be the case. The start of cure advanced 50 per cent, and rate of curing speeded about 10 per cent. The factice employed in this experiment had a "free" sulfur content of 4.5 per cent, and it is reasonable to assume that this accounts for the greater vulcanizing activity, though it seems to be general experience that the "free" sulfur is not entirely free, and cannot be fully depended upon in vulcanization.

Tetramethylthiuram disulfide and Clay.—Clay on the other hand was found to have an antiscorch effect. Thirty per cent of Spestone, the only clay available, with 2 per cent of T.M.T. delayed the onset of cure by 30 per cent, but thereafter the rate of curing was unaffected. It therefore suggests itself as a suitable filler with this accelerator.

Tetramethylthiuram disulfide and Carbon Black.—Channel black (Micronex) up to 30 per cent with 2 per cent T.M.T. had no appreciable effect on the commencement or rate of cure.

Tetramethylthiuram disulfide and Antioxidant.—Two per cent of an antioxidant with 2 per cent of T.M.T. (Nonox-S) was found to delay the time of scorching by approximately 10 per cent, and to exercise a slight retarding effect on the rate of curing.

General Notes.—Mention has already been made of the absence of sulfur bloom on rubbers accelerated with thiuram disulfides and that, as a consequence, these rubbers have no corrosive effect on metals. It is interesting, therefore, to note that, of all the common accelerators, thiuram disulfides give the poorest rubber-to-metal bond, and it seems reasonable to assume that free sulfur plays an important role in this respect.

It is understood that, in the manufacture of certain types of GR-M, T.M.T. is added as a polymerization inhibitor to prevent after polymerization; one type (believed to be GN), when tested by the method described later (under "Detection"), gave a positive result, indicating the presence of T.M.T. This possibility must be borne in mind in the manufacture of composite articles where natural rubber and GR-M compounds come in contact, or when rubber and GR-M are mixed, as the T.M.T. may migrate from the GR-M into the rubber and if the latter contains an accelerator which is readily boosted by T.M.T., then rapid aging may result.

The presence of T.M.T. with zinc oxide in rubber has been shown[1] to act as a fungicide, this feature being largely retained even after vulcanization, and the property may be useful in articles containing textile components, which form a happy breeding ground for bacteria.

Detection of Thiuram Sulfides in Rubber.—Thiuram sulfides are converted during curing to zinc dialkyldithiocarbamates and the method of detection is based on this fact and on the sensitive color reaction between copper and

dithiocarbamates. A rapid test was devised, and for simplicity of explanation is best regarded in two steps as follows.

(1) A few grams of the rubber to be examined is reduced, by cutting or milling, to expose the maximum of surface, is placed in a test-tube, and shaken with a little chloroform for a few minutes. The extract is then decanted into a second tube, and two drops of copper oleate solution added. A distinct golden to brown coloration indicates the presence of dithiocarbamate. Mercapto-benzthiazole and(or) diphenylguanidine do not interfere.

(2) If in (1) no coloration is obtained, a few cc. of saturated aqueous sodium sulfite solution is added with shaking. Any thiuram sulfide present will be reduced to dithiocarbamate and cause a coloration as described. Sulfite was found preferable to other reducing agents, such as sulfur dioxide or nascent hydrogen, for it is convenient and provides a good background to the coloration by reason of the white turbidity produced when shaken with chloroform.

Test (1) indicates the presence of dithiocarbamate, but does not show whether this was added as such originally, or was derived from the reaction of thiuram sulfide during curing. It was hoped to devise a test which would detect residual thiuram sulfide, though this could only be expected to exist in undercured or heavily overaccelerated rubbers. Trial of several tests to detect thiuram sulfide in the presence of dithiocarbamate was unsuccessful, the latter causing interference, and an attempt was then made to separate the two by extracting a chloroform solution containing them both with dilute caustic soda solution. It was hoped, thereby, that the dithiocarbamate would be dissolved out by the soda, leaving the thiuram in the chloroform, but even after repeated extractions the chloroform retained a considerable amount of dithio-carbamate, and the problem remains to be solved.

However, the employment of thiuram and dithiocarbamate accelerators together in a mix is not likely, and the nature of the goods under examination would probably give an indication as to which was originally incorporated.

These tests can be employed to show whether an unvulcanized stock contains thiuram sulfide and as a rapid method to detect scorching of such a mix (provided no dithiocarbamate was originally incorporated), *i.e.*, if on applying test (1) a golden coloration is obtained, then thiocarbamate is present and can be derived only from the thiuram sulfide due to commencement of vulcanization. When the test was applied to the test-pieces, from the scorch curves already shown, in each case the formation of dithiocarbamate coincided with the first upward movement of the curves. This provides some verification for the theory of thiuram vulcanization and proves the usefulness of the test as an indication of scorching.

The foregoing applies, of course, to the thiuram mono-, di- and polysulfides.

The copper oleate solution was prepared by placing 2 grams of oleic acid and 5 grams (an excess) of copper carbonate in a test-tube and heating in a water-bath for an hour, shaking occasionally. The copper oleate was then extracted by adding 100 cc. of chloroform, shaking and decanting from the residue of copper carbonate. This chloroform solution was used in all tests, and appears to keep indefinitely.

It has been stated that mercaptobenzothiazole does not interfere with the method of detection given above, although mercaptobenzothiazole gives a golden or brown precipitate with copper oleate. The statement is based on the fact that 50 mg. of M.B.T. added to 10 cc. of a chloroform solution of copper oleate merely changed the color from green to light yellow, whereas 1 mg. of

T.M.T. gave a distinct golden-brown coloration.   It is extremely unlikely that more than 50 mg. of M.B.T. would be extracted, and therefore M.B.T. may be ignored as a possible substance capable of interfering with this qualitative test.

ACKNOWLEDGMENT

In conclusion, the authors wish to thank the Craigpark Electric Cable Co., Ltd., for permission to present this paper.

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ACCELERATED OZONE WEATHERING TEST FOR RUBBER *

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It has been previously shown by the authors[1] that two separate and distinct factors are responsible for the changes which rubber compounds undergo when exposed outdoors: a light-energized oxidation and attack by ozone which is normally present in the atmosphere in minute concentration. The former acts independently of stress in the rubber, the latter only when the material is stretched.

Since sunlight, ozone, and temperature vary hourly, daily, seasonally, and with locality, the overall result to the exposed material depends on the balance between the causative factors and is unique, since any given combination of such factors is not duplicated. It is, therefore, essential that the susceptibilities of a given compound to damage by these two factors be determined separately. The information thus furnished will then make it possible to estimate the durability of the compound under any given set of conditions.

Damage by light-energized oxidation can be mitigated to any great extent only by physical protection from light, which can be partially achieved by incorporation of carbon black or ferric oxide. It is likely to be the major factor in the case of light-colored goods. Susceptibility can be readily gauged by measurement of the oxygen absorbed when the material is irradiated in air or oxygen under controlled conditions. The present obstacle to formulation of a standard test is the lack of a constant and reproducible light source which simulates sunlight.

This article is principally concerned with the ozone factor. In the case of rubber goods containing appreciable loadings of carbon black, such as insulated cable jackets and hose, by far the most important cause of deterioration is the familiar cracking at stressed locations by the ozone of the atmosphere, popularly and erroneously referred to as "light cracking".

Many workers have attempted to use ozone-cracking in the laboratory as a measure of outdoor-cracking, only to abandon the method because of failure to duplicate outdoor ratings. The probable cause of this failure has been found by the authors to be the use of too high concentrations of ozone. Small additions of wax, for example, which would confer substantial protection to cracking at atmospheric concentrations of ozone, are quite without effect in most cases at concentrations one hundred times greater. If ozone concentrations approximating that of the atmosphere be used (around 3 parts per 100,000,000 by volume) outdoor exposures can be closely duplicated. Rubber compounds designed principally for wire and cable insulations for outdoor use have been rated in this way in these laboratories for some time with considerable success.

The nature and degree of cracking of a given compound on exposure to dilute ozone depend on the concentration, the temperature, the degree of elongation, and whether this is static or dynamic[1].

TEST CONDITIONS

For accelerated aging in the laboratory the authors have currently adopted a concentration of 25 ± 2 parts of ozone per 100,000,000 of air by volume as the test atmosphere and the expiration of time for the first appearance of cracks in the stressed sample at the chosen degrees of elongation (usually 20 and 30 per cent) and temperature as the measure of performance. The specimen is examined under magnification of 7 to 10 times, which not only gives results more quickly but greatly reduces errors due to any visual defects of the observer.

Ozone concentrations up to 100 parts per 100,000,000 can be satisfactorily used in many cases of highly weather-resistant compounds but are not permissible for general use. Unfortunately in ozone at 25 parts per 10^8, the time taken to crack such compounds at room temperature is too long to be practicable for an accelerated test; so resort is taken to the effect of increased temperature.

In the absence of protective wax, increase in temperature results in more but much finer cracks which in many cases can be recognized only under magnification. In the presence of wax, cracks when formed are few but large and well defined. Raising the temperature reduces progressively the effects of the waxes in current usage until a point is reached at which they are ineffectual. For a given wax this temperature increases with its concentration, and is higher for GR-S compounds than for natural rubber compounds. For example, a GR-S cable jacket, a natural rubber cable jacket, and a natural-rubber gum compound containing various additions of a certain wax, at 25 per cent elongation in an ozone atmosphere of 25 parts per 100,000,000, gave the results shown in Table I in hours to crack.

TABLE I

EFFECT OF TEMPERATURE ON TIME TAKEN TO CRACK

Compound	Wax %	Temperature, degrees Fahrenheit					
		80 Hours	110 Hours	120 Hours	130 Hours	140 Hours	150 Hours
GR-S cable jacket	0	10	3	1	1	1	1
	1	72	5	2	1	1	1
	2	400	30	6	2	1	1
	3	*	*	18	5	2	1
	4	*	*	60	20	3	2
	5	*	*	240	60	8	3
Natural rubber cable jacket	0	3	1.5	1	1	..	..
	1	100	2	1	1	..	..
	2	300	4	1	1	..	..
	3	450	40	1	1	..	..
	4	†	60	1	1	..	..
	5	†	85	2	1	..	..
Natural rubber gum compound	0	4	2	1	..	..	..
	1	110	3	1	..	..	..
	2	200	3	1	..	..	..
	3	340	4	1	..	..	..
	4	‡	5	1	..	..	..

* Good after 6 months.
† Good after 3 months.
‡ Good after 1 month.

These values, plotted in Figures 1, 2, and 3 on a semilog basis, reveal a distinct connection between temperature and wax content. As the tempera-
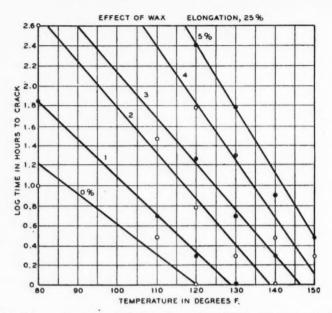
FIG. 1.—Effect of temperature on time taken to crack a GR-S cable jacket compound containing different amounts of protective wax. Ozone concentration 25 parts per 10^8, elongation 25 per cent.
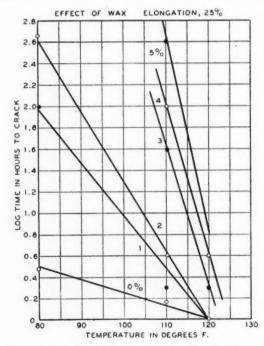
FIG. 2.—Effect of temperature on time taken to crack a natural rubber cable jacket compound containing different amounts of protective wax. Ozone concentration 25 parts per 10^8, elongation 25 per cent.

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ture rises, a progressive decrease in cracking time occurs, the gap between low and high wax additions being gradually closed, more rapidly in the case of natural rubber compounds than in GR-S compounds. It is this feature that is suggested as the basis of accelerated testing of susceptibility to atmospheric ozone cracking. The temperature of test chosen for a given type of compound is such that the highest economically practicable addition of protective wax can
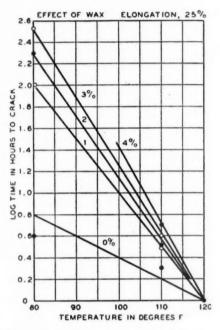
FIG. 3.—Effect of temperature on time taken to crack a natural rubber gum compound containing different amounts of protective wax. Ozone concentration 25 parts per 10^8, elongation 25 per cent.

be made to fail in a reasonable time, say 3 or 4 days. This temperature is obviously lower for natural rubber than for GR-S, 70° to 80° and 110° F being suggested for the former and 120° or 125° for the latter. The proposed concentration of ozone is 25 to 30 parts per 100,000,000 and the degree of elongation 20 or 25 per cent. The criterion of performance is the time taken for the first sign of cracking to appear.

It is not suggested that the ratio of performance between low and high wax additions remains the same with change in temperature, so the lower temperature life may be determined by extrapolation from the higher. Compounds of known weathering performance must be used as controls. It is considered that as data accumulate over a wider range of compounds it will be possible to establish definite performance requirements under specified conditions similar to those outlined above. The room temperature test is intended to cover compounds of low weathering resistance and to detect anomalies, as, for example, a certain wax examined by the authors which is actually highly efficient at 120° F but performs poorly at room temperature (Figure 4).

TEST APPARATUS

Essential to the test are means of furnishing and maintaining uniformly an atmosphere of ozone of the required concentration. This is readily and most conveniently accomplished by passing air or oxygen over a mercury vapor lamp having an envelope of quartz or glass transmitting short-wave ultraviolet light. Ozone is formed from the oxygen by the short-wave ultraviolet light. For laboratory use modifications of the apparatus shown in Figure 16 of the previous paper[1] are used. With this arrangement a flow ranging up to 1 cubic meter of air per hour can be supplied at concentrations from 5 to several hundred parts of ozone per 10^8. The higher the flow, the lower the concentration. The ozone produced decreases rather rapidly at first but more slowly after a hundred hours or so, permitting a very uniform output, providing temperature
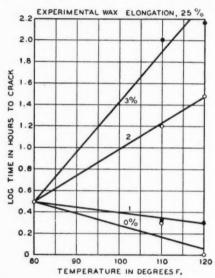
FIG. 4.—Anomalous behavior of an experimental wax-natural rubber gum compound.
Ozone 25 parts per 10^8, elongation 25 per cent.

and voltage are kept uniform the humidity of the air supply has no extreme variations. The lamps should burn continuously. Used in this way they function for several months.

In the past the authors have made considerable use of the G.E. germicidal lamp as ozone generator, since the yield is much less and easier to control than with the quartz tube. However, the nature of the glass in this lamp has recently been modified so as to reduce the ozone output, making it practically useless as an ozone generator. The lamp in current use for the purpose is the Hanovia Safe-t-aire lamp, a mercury vapor discharge tube in quartz. This lamp (Catalog No. 2851) has normally a 30-cm. (12-inch) column and, even when operated at as low a voltage as possible, generates far too much ozone for easy control. The output can, however, be regulated nicely by covering part of the column with aluminum foil or other opaquing means. Only about 5 cm. (2 inches) of exposed column are needed for a laboratory generator. The tube is held concentric by waxed or shellacked corks or rubber stoppers in a glass tube 2 or 3 inches in diameter provided with side tubes for inlet and outlet of air. This lamp operates at a low temperature and has a very long life. [Currently

(August, 1946) a small 12-volt lamp recently developed by the Westinghouse Electric Corp. (Sterilamp WL-794) is being tested.   This lamp, of automobile headlight bulb size and intended for use in household refrigerators, is a most convenient source for a laboratory generator delivering from 0.5 to 1.0 cubic meter per hour.   Not enough experience has been gained to determine its useful life.]

The flow of ozonized air from these generators is conducted to the base of a laboratory-type oven maintained at the temperature at which the specimens of rubber are to be exposed.   Suitable baffles should be installed to ensure uniform flow at all parts of the oven, and the inside should be well varnished
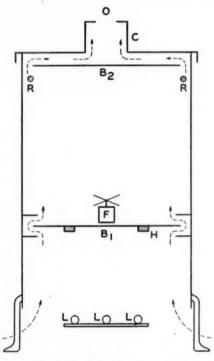
Fig. 5.—Schematic drawing of test chamber.

or waxed, since rapid decomposition of ozone occurs at metal surfaces.   Even so the concentration in the oven is less than that from the generating apparatus and should always be measured at the location of the specimens.

Where large numbers of specimens are to be exposed a different arrangement is used, as depicted schematically in Figure 5.

This consists of a drum or tank, 2 feet in diameter and 3 feet high on legs, open at the bottom and closed at the top, with a loosely fitting lid furnished with a short chimney.   The inside is divided into 2 compartments by baffle B_1 12 inches from the bottom.   This baffle is 2 inches less in diameter than the drum, the two rings shown acting as a light-lock to prevent light from reaching the upper chamber.   Another similar baffle is mounted just below the lid. The lower chamber houses an aluminum plate, on which is mounted a single Hanovia No. 2851 Safe-t-aire lamp operated, after aging for a few hundred

hours at approximately 750 volts alternating current. Ozone in suitable concentration is thus generated in this chamber. This air rises into the upper chamber through the opening between the edges of baffle B_1 and the sides of the drum, escaping to the outer air around baffle B_2 and through the chimney, C. The amount and concentration of air thus circulating can be readily controlled by adjusting the size of the opening, O, of the chimney or installing a damper in the chimney. A small fan rotating slowly on reduced voltage may advantageously be mounted on baffle B_1 to ensure uniformity of composition and temperature of the air in the upper chamber. The fan blades should be adjusted to generate only a horizontal disturbance.

If the device is to be operated at an elevated temperature, a ring heater is mounted on the underside of baffle B_1, regulated by a thermostat mounted in
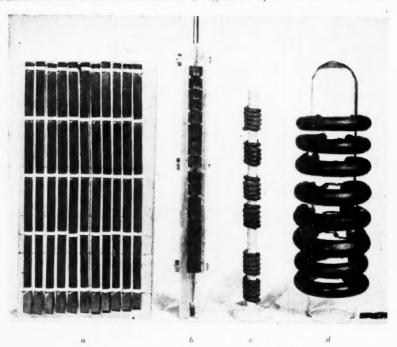
FIG. 6.—Methods of mounting stretched specimens for test.

the upper chamber. A 500-watt heater will maintain a temperature of 110° F and a 750-watt heater a temperature of 120° F. When used at these elevated temperatures, the drum is insulated with a layer of thick felt or other suitable material. The specimens to be exposed are suspended by wires from rail R around the inside walls of the upper chamber. The drum should be preferably of aluminum, which is less active as a decomposition catalyst of ozone than copper, iron, or zinc. In any event the inside should be painted with a thin layer of wax. In the units used in these laboratories a full chimney opening gives a concentration of ozone in the upper chamber of 25 parts per 10^8, using the lamp referred to. The opening is reduced in size as the activity of the lamp decreases with age.

Specimens for exposure are mounted as shown in the photograph of Figure 6.

Sheets are mounted as strips stapled to a waxed board, *a*, at elongations chosen, usually 20, 25, 30, and 50 per cent, though GR-S compounds usually break at the staple with 50 per cent elongation. Alternatively strips are mounted bent around a mandrel of a diameter calculated to give the required elongation, the ends secured between 2 wooden strips, *b*. Wires, *c*, are wound around waxed dowels or glass rods of the necessary diameter and cables, *d*, similarly wound on glass tubing. Specimens must not be exposed immediately after mounting, but must stand for a uniform time of at least 24 hours to allow healing of any wax film that may have been disrupted by the stretching. Comparison between sample and control should be on the basis of identical mountings. Sheets should not be compared with wires, for example.

MEASUREMENT OF OZONE CONCENTRATION

The above procedure is of little value without a means of determining the concentration of the ozone in the atmospheres in the exposure chambers. In the routine operation of several of the accelerated weathering devices described, a simple and rapid method of estimation had to be devised, because, although with careful attention to air flow, voltage, and temperature, uniform concentrations can be maintained, ozone is an unstable substance, and assurance of a uniform concentration can be had only by repeated checking at reasonably close intervals, at least daily. Moreover, the answer must be obtainable within a relatively short time, not more than an hour. The ideal method would be by measurement of ultraviolet-light absorption in the region of the ozone absorption band having a peak at 2,550 Å. However, at the concentrations of ozone in use this would call for a path at least 50 feet long to give a practicable measure and is thus inconvenient.

The method currently used reverts to the classical method of estimation by absorption by a solution of potassium iodide in water and estimation of the iodine liberated. To furnish sufficient iodine for measurement in the short time allotted a large volume of air must be dealt with. To ensure absorption of the ozone, the air to be measured is made to generate a fine spray of potassium iodide solution. In this way an enormous surface of solution is furnished for the reaction. The apparatus is shown schematically in Figure 7 and illustrated in Figure 8.

In Figure 7, *A* is a glass tube 0.375 inch in diameter (approximate) and about 4 inches long, terminating at *B* in a short length of capillary tubing with a bore of 1 to 2 mm. Concentric within *A* is a smaller glass tube, *C*. (Figure 7, *a*, shows this assembly on a larger scale.) The end of *C* is first carefully heated in a blowpipe flame till the bore is reduced in size so as just to admit a No. 69 drill. At this thickened end two flats are ground off on a sheet of fine Aloxite paper as at *D* in Figure 7, *b*. When in position in tube *A*, end *D* fits snugly against the hole in capillary *B*. *C* may now be sealed to *A* at the upper end, but it is better to rely on the rubber connection at *E* to hold the tubes in place, since once sealed in, *C* cannot be removed for cleaning in the event of a blockage.

F is a trap about 2 inches in diameter and 4 inches long, requiring no further description, and *G* is an enlargement in the exit tube, about 1.5 inches in diameter, containing glass wool to trap spray passing *F*. *F* is connected to the side tube of *A* by rubber tubing or may be permanently attached, as shown in the figure. The rubber connector is more convenient, but the tubing used must first be soaked for a long period in dilute iodine solution and thoroughly washed, or iodine may be taken up from the reagent. *H* is a 1-liter three-

necked Woulff bottle in which A and F are secured by Pyrex ground joints, A occupying the center opening with B protruding just below the neck and tube J reaching to within 0.5 inch of the bottom of the bottle. The third neck serves to introduce and remove the reagent.

A is connected through rubber joints and glass or plastic tube K to rotameter L, graduated from 0 to 1.0 cubic meter of air per hour. The entrance to the rotameter is connected to the atmosphere whose ozone content is to be determined, and the exit from F is connected to a vacuum line. After 75 cc. of
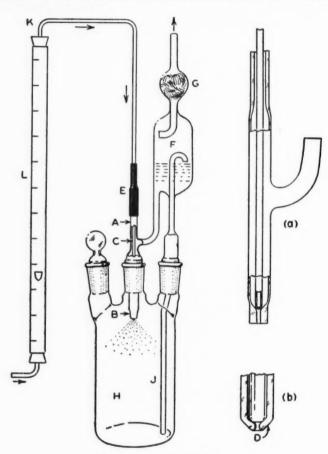
FIG. 7.—Ozone-absorbing device.

reagent are introduced into H, the stopper is replaced, and the vacuum gradually applied. Almost the entire body of liquid enters F, furnishing a head of reagent at B, where the entering air resolves it into a fine mist which fills the entire bottle. At the end of the run the vacuum is disconnected and the liquid transferred to the titration vessel. For atmospheres containing around 25 parts of ozone per 10^8 of air, ample iodine for titration is obtained in 0.5 to 1 hour. When runs longer than 1 hour are called for, it is necessary to add distilled water at intervals to make up for evaporation. This is most conveniently done through the air intake. The liberated iodine is determined by titration with

sodium thiosulfate. Since the amount is so small, 0.002 N to 0.001 N solutions must be used, and since the end point using starch as indicator is uncertain, the electrometric method of Foulk and Bowden[2] is resorted to, in which use is made of the depolarizing effect of iodine on a polarized electrode.

In the authors' practice the titration vessel is a 250-cc. wide-mouthed extraction flask having a hole in the side near the neck. A two-hole rubber stopper carries into the flask 2 glass tubes into which are sealed the two electrodes, in this case stout platinum wires (0.1 inch thick) with circular loops at the ends to increase the areas exposed to the liquid. Sensitivity is increased by increasing the surface area of the electrode, but this form is used because it is
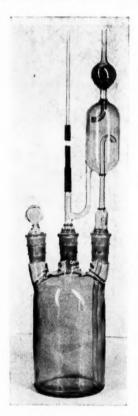
Fig. 8.—Ozone-absorbing device.

rugged and not disturbed by agitation of the liquid. A potential of 30 to 40 millivolts is applied to the electrodes. This is readily obtained by connecting suitable resistors—e.g., 30,000 and 1000 ohms—in series across an ordinary 1.5-volt dry cell and picking off the voltage across the resistor of lower value. A galvanometer is connected in series. The authors use a Rubicon 3402-H.H. with an Ayrton shunt, but a less sensitive type is probably sufficient.

Fifteen grams of potassium iodide are dissolved in 75 cc. buffer solution (equal volumes of 0.025 N disodium hydrogen phosphate and 0.025 N potassium dihydrogen phosphate). The solution is introduced into the titration flasks, the electrodes are inserted, and the liquid is swirled vigorously over them.

Following an initial kick the galvanometer spot returns to zero if no iodine is present, because polarization of the electrodes prevents passage of current. The presence of an oxidizing agent such as iodine removes the polarizing hydrogen from the cathode and current flows. Addition of thiosulfate (through the hole in the side of the flask) until the iodine is removed restores the polarized state and returns the galvanometer deflection to zero. The reagent usually requires the addition of 2 to 5 drops of 0.002 N thiosulfate, depending on the batch, to bring this about.

After the ozone run the iodide solution containing the iodine is placed in the titration vessel and thiosulfate is added until only a barely perceptible yellow remains; then the electrodes are inserted and thiosulfate is added drop
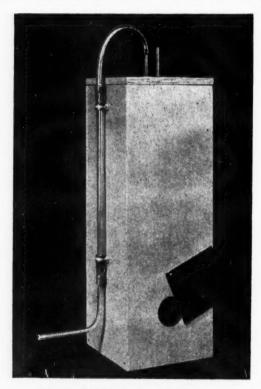
Fig. 9.—Dark housing for ozone absorber.

by drop at intervals until no deflection is obtained; the liquid is vigorously swirled meanwhile. The liquid is then returned through the trap to rinse the apparatus and the titration is completed. One cc. of 0.001 N thiosulfate represents 0.0112 cc. of ozone at S.T.P.

A little difficulty may be encountered at first in identifying the end point to within one drop of thiosulfate solution at this low concentration. It will be found easier if the titration is made to a small residual deflection of the galvanometer.

Neither the form nor dimensions of the apparatus described are critical. Those given are of the apparatus in current use. Duplicate apparatus reproduces results within ±5 per cent, which is good enough at these low con-

centrations. It has been found that reducing the concentration of the potassium iodide solution below 20 per cent gives low results. The system described passes about 0.3 cubic meter of air per hour, but this can be changed by changing the size of the air jet, C. With a given jet there may be considerable leeway in the size of the capillary nozzle. The criterion is a reaction vessel filled with a mist of reagent. The authors have compared reaction vessels ranging in size from 125 cc. to 12 liters, and find a tendency to low results with a capacity of less than 500cc. A larger vessel than this yields no advantage.

A most important point to remember is that potassium iodide in solution is photochemically oxidized to iodine in presence of light, even in neutral or alkaline solution. Therefore titration must not be conducted in bright daylight, and during the ozone run the whole of the absorption apparatus must be enclosed in a light-tight box as shown in Figure 9. Failure to observe this precaution will result in utterly erroneous findings.

The 0.002 N thiosulfate should be standardized at frequent intervals, as such dilute solutions lose strength through oxidation.
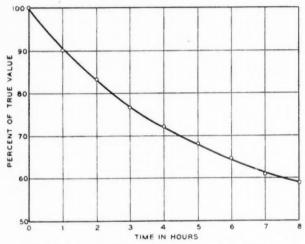
FIG. 10.—Correction curve for ozone estimation described in text.

Since the iodine in solution has a vapor pressure, some is carried away in the exhausted air; a correction must therefore be applied to the result obtained. The amount of this has been determined in two ways: (1) by making determinations over a range of increasing periods of time, plotting the ozone found against time, and extrapolating to zero time which gives the true value; (2) by operating the apparatus with a stream of nitrogen and simulating the ozone reaction by adding small amounts of 0.001 N iodine at frequent intervals over the desired period and in amount equivalent to the ozone concentration studied. Comparison of the iodine remaining in solution with the amount added gives the error. These two methods checked each other within ±5 per cent at any concentration between 3 and 25 parts of ozone per 10^8. The percentage loss with time is shown by Figure 10. The determinations were made over a period of only 2 hours at the highest concentration, since measurement time in practice never exceeds 1 hour. With decreasing concentration the period was increased progressively up to 8 hours for the lowest.

The curve applies only to the particular conditions employed—*viz.*, a flow

of 0.27 to 0.30 cubic meter per hour and a vacuum of 60 cm. of mercury.   For other conditions the correction must be determined experimentally.

The absorption of ozone is assumed to be complete, since increasing the concentration of potassium iodide up to 80 per cent gave no higher values. Further, dilution experiments, in which ozone of concentrations up to 100 parts per million was diluted with a known volume of air and the dilution simultaneously measured, when carefully conducted, checked within ±5 per cent.   This is not a definite proof but a reasonable assumption.

It might be thought that the loss of iodine could be reduced by cooling the reaction vessel in ice.   The reduction has proved on trial to be insignificant. Expansion of the air at the nozzle and some evaporation of the water results in cooling the reagent to around 60° F, depending on the duration of the run. Where room temperatures are high as in summer months, however, immersion in ice would ensure more uniform conditions.

The principal merit of this method lies in the rapidity with which ozone concentrations at the level suggested for use in the accelerated weathering methods described can be made.   Since variations in the rubber compounds tested and personal errors in recognizing the first appearance of cracking are often large, it is felt that this method is well within the overall accuracy possible in weathering values.   It is planned to check the method further against light-absorption determinations.

An apparatus for the continuous recording of ozone concentration, employing the above principles, has been described by Gluckauf, Neal, Marten and Paneth[3].   The output of such an apparatus could readily be arranged to maintain a constant concentration of ozone in a test chamber by adjustment of the voltage to the ultraviolet lamp.   It is possible, however, that the effort involved in maintenance of such apparatus would exceed that called for by intermittent control in the procedures described in this paper.

In the measurement of ozone concentrations of the atmosphere by the potassium iodide reaction, the criticism is often advanced that other oxidizing agents known to be present also liberate iodine from potassium iodine.   These are nitrogen oxides, hydrogen and other peroxides, and chlorine.   However, Gluckauf, Neal, Marten, and Paneth[3] point out that the reaction producing iodine:

$$NO_2 + 2H^+ + 2I^- \rightarrow H_2O + NO + I_2$$

proceeds only to a very limited extent at low concentrations and at pH 7.0, because of the lack of hydrogen ions and prove this by experiment.   The present authors have found by trial that nitrogen peroxide even in concentration three- or fourfold that of the atmosphere[4] does not liberate iodine from potassium iodide by the procedure described.   As for hydrogen and other peroxides, the authors have made repeated attempts to trap suspended particles of organic peroxides in a water spray and to freeze out hydrogen peroxide in traps cooled by a dry ice–acetone bath.   The liquids so obtained from several cubic meters of air have invariably failed to liberate titratable amounts of iodine from buffered potassium iodide solution.   Free chlorine apparently is absent from the atmosphere at the location of these laboratories.   Nevertheless, in this connection the possibility of the presence of these or other oxidizing agents in the atmosphere of industrial locations should be borne in mind.

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EFFECT OF METALLIC POISONS, ESPECIALLY MANGANESE, ON AGING OF VULCANIZED NATURAL RUBBER *

RESEARCH ASSOCIATION OF BRITISH RUBBER MANUFACTURERS

INTRODUCTION

The present report is concerned mainly with manganese, but includes some observations on copper.

Although the harmful effect of manganese on aging was first observed fifty years ago, the mechanism of its action is still imperfectly understood and, what is of more immediate importance to the practical man, it is not possible to predict, from the manganese content of a compounding ingredient, whether it will cause bad aging or not. Published statements as to what is a dangerous proportion, including limits given in specifications, vary so widely as to give little guidance. Thus, the A.S.T.M.[1] limits the manganese in fabrics for proofing to 0.0005 per cent, while Kluckow and Siebner[2] state that fillers and fabrics should not contain more than 0.005 per cent. Stevens[3] considers that more than the (approximately) 0.0003 per cent each of copper and manganese normally present in the raw rubber may promote deterioration. On the other hand, Esch[4] considers 0.007 per cent of manganese present as carbonate in whiting to be harmless, and 0.005 per cent of manganese has been permitted in white used for certain British Government specification goods. Kirchhof[5], however, states that 0.05 per cent on the rubber is dangerous, and found a filler containing 0.15 per cent to give bad aging even in presence of an antioxidant. Whiting containing 0.02 per cent manganese is stated to be harmless, but the same amount of manganese added as sulfate leads to a rapid aging of the rubber[6]. Kieselguhr containing 0.02 per cent of manganese had very little, if any, harmful effect on aging[7].

Sackett[8], studying the aging of vulcanizates made from raw rubbers of various manganese contents, found that 0.004 per cent increased the rate of deterioration of accelerated "pure gum" stocks (without antioxidant) by about 50 per cent, while 0.022 per cent at least doubled the rate. The manganese had a smaller, but still noticeable, effect in rubber-sulfur and tire-tread stocks, and addition of an antioxidant lessened the effect. Hastings and Rhodes[9] found that using water containing 220 parts per million of manganese for soaking coagulum before drying accelerated the deterioration of the vulcanizate by some 50 per cent, but the manganese content of the rubber was not stated. (This same manganese-containing water was apparently the source of the manganese in the rubbers studied by Sackett.) Taylor and Jones[10] found that in a tread stock as little as 0.1 per cent of manganic oleate (equivalent to 0.006 per cent of manganese) on the rubber was harmful to aging.

The problem of harmful impurities became more important during the war, owing to the necessity for using fillers of new types or from new sources, which

might contain them in greater quantities than the well-tried materials hitherto in use. A fuller knowledge of the effects of these impurities, in various amounts and different forms of chemical combination, would be useful both in helping to avoid unsafe materials and in making it possible to use with confidence materials now regarded with suspicion.

The harmful effect of copper is known to vary enormously according to the form in which it is present[11], and it is, therefore, important to establish whether this is true also of manganese. As little precise information on this point is available, it was decided to study the matter, because it would appear that, if the activity of manganese does depend largely on its state of chemical combination, the manganese content of fillers would then be in itself of little significance, and much trouble might be saved by eliminating unnecessary analyses.

While this work was in progress it was further decided, as a step towards giving the investigation a more directly practical value, to ask Member firms of the R.A.B.R.M. to give the Association any information on cases of bad aging known or believed to be due to metallic poisons, or any other relevant facts. The replies to this inquiry proved interesting in showing that manganese compounds are less harmful than is usually thought. It is, therefore, believed that a summary of the information given will be of general interest; the present report contains such a summary, together with the results of the experimental investigation.

SUMMARY OF INFORMATION FROM MEMBER FIRMS

In response to a circular letter addressed to Members in 1942, replies were received from eleven firms, comprising mainly general, tire and cable manufacturers.

Two replies stated that during the war period the manganese contents of fillers, especially whiting and French chalk (or alternative talcs), had increased. Examples of excessive manganese contents met with are: Canadian talc 0.10 per cent, asbestos powder 0.075 per cent, barytes 0.035 per cent, and treated calcium carbonate 0.055 per cent; though these were the exception rather than the rule. Oven-aging tests on rubbers containing such fillers, however, showed little sign of any adverse effects. One firm found up to 0.10 per cent of manganese in slate powder, and because of this and its high iron content did not adopt it for general use.

In line with this evidence of the comparative inertness of traces of manganese is the statement by a tire manufacturer that manganese up to 0.05 per cent and copper up to 0.005 per cent in fillers similar to whiting have no harmful effect when using up to 13 volumes of filler per 100 of rubber; if only one of the metals is present the amounts may be as high as 0.07 and 0.008 per cent, respectively, and in presence of a good antioxidant far greater amounts can be tolerated.

It is the general opinion that copper seldom occurs in dangerous amounts in compounding ingredients; one firm found that copper contents had tended to increase, though without any apparent ill effect on aging. The only example of copper poisoning quoted related to a baryte containing 0.016 per cent copper, which gave bad aging in a cold-vulcanized proofing.

Apart from the case just quoted, none of the replies refers to any difficulty known or suspected to be due to manganese or copper in the fillers then in use. Two of the replies, indeed, express the definite opinion that these metals are not always so harmful as has hitherto been believed.

EXPERIMENTAL INVESTIGATION

It was decided first to examine various inorganic manganese compounds, including the commoner manganese minerals, that is, the forms in which manganese is likely to occur in such fillers as whiting, clay, barytes, slate, or talc. The minerals examined were pyrolusite (MnO_2), psilomelane (Mn_3O_5), manganite (Mn_2O_3, H_2O), rhodocroisite ($MnCO_3$), and rhodonite ($MnSiO_3$).

Each compound was added, in quantity equivalent to 0.01 part of manganese, to a base stock of smoked sheet 100, sulfur 2.5, barytes 75, zinc oxide 5, stearic acid 1, mercaptobenzothiazole 0.75.   To obtain good dispersion, the manganese compound was finely powdered and then intimately mixed with 1.5 parts of the barytes by grinding in a mortar; the whole was then milled into 20 parts of the rubber.   The remaining ingredients were master-batched, and the batch was divided and blended with the manganese batches.   Sheets 0.1 inch thick, vulcanized for 25 minutes at 141° C, were used for tensile tests before and after various periods of Geer and oxygen bomb (70° C and 300 lbs. per sq. in.) aging.

TABLE I

PROPERTIES BEFORE AGING

Mix	Manganese compound	Tensile strength (lbs. per sq. in.)	Elongation at break (%)	Modulus (lbs. per sq. in.) 500%	700%
A	(none)	2475	750	640	2025
B	manganous sulfate*	2650	760	580	2000
E	manganic oxide	2650	790	480	1750
F	manganese dioxide	2800	780	600	1925
G	manganous chloride*	2650	770	560	1950
H	manganous sulfide	2700	770	580	1950
J	manganous carbonate	2825	780	620	2050
K	psilomelane	2925	780	620	2050
L	pyrolusite	2700	770	580	1950
M	manganite	2925	780	620	2050
N	rhodocroisite	2675	760	560	1975
P	rhodonite	2720	760	580	1975

* anhydrous.

Table 1 shows some differences in tensile strength before aging, notably with A (low) and K and M (high), but as these largely disappear after the first aging period (see Table 2), they may represent experimental errors rather than real differences.   Apart from Mix E, all the rubbers give closely similar moduli.

TABLE 2

TENSILE STRENGTH (LBS. PER SQ. IN.) AFTER AGING

Mix	Days in Geer oven 7	12	20	35	Hours in bomb 24	48	96
A	2650	2075	2125	1450	2275	1600	1550
B	2500	2150	2050	1450	2200	1775	1400
E	2400	2350	2150	1625	2275	2075	1750
F	2375	2050	1875	1475	2200	1775	1075
G	2775	2600	2275	1825	2350	2225	1075
H	2650	2450	2150	1450	2400	2075	1250
J	2450	2375	2350	1775	2400	2050	1925
K	2700	2625	2200	1875	2625	2075	2025
L	2725	2525	2350	1950	2500	2300	1575
M	2300	2450	2020	1720	2525	2250	1325
N	2425	2300	2075	1625	2250	2050	1425
P	2625	2525	1850	1550	2300	2250	1625

In the aging results (Table 2) only tensile strength has been given, since the changes in modulus were much the same for all the rubbers.

It is clear that none of the manganese compounds caused really bad aging, since all the rubbers maintained tensile strengths of at least 1,450 lbs. per sq. in. (45 per cent below the unaged value) after 35 days in the oven, and at least 1,075 lbs. per sq. in. (60 per cent below unaged) after 96 hours in the bomb.

In studying the data more closely to detect any effect of the manganese, the results were first expressed as the cumulative loss in strength over the aging period, that is, the area between the aging period/strength curve and a horizontal line through the initial (unaged) strength value. The possibility that differences in initial strength might arise from experimental error introduces some uncertainty into this method, as indeed into any method based on the comparison of aged with unaged values. If the differences are due entirely to experimental error, the average of all the initial values should be used as the datum line for each mix, whereas if the differences are real, the results for each mix should be related to its own initial value. The data have, accordingly, been examined in both these ways, and are referred to respectively as (a) and (b) in Table 3.

TABLE 3

RELATIVE RATES OF DETERIORATION (MIX A = 100)

Mix	Manganese compound	(a)	(b)	(c)	Mean
L	pyrolusite	60	75	75	70
G	manganous chloride	70	80	95	80
K	psilomelane	60	105	85	85
J	manganous carbonate	70	105	80	85
E	manganic oxide	80	100	85	90
P	rhodonite	85	115	95	100
N	rhodocroisite	90	115	95	100
H	manganous sulfide	85	110	115	105
M	manganite	80	135	100	105
B	manganous sulfate	105	130	105	115
F	manganese dioxide	115	160	120	130

An alternative method, which avoids this difficulty, is to take the slope of the aging/strength curve, which can readily be estimated because most of the curves happen to be approximately linear; this is method (c) in Table 3. The oven and bomb tests were found to arrange the rubbers in much the same order, and can therefore legitimately be averaged together. By so doing the three sets of figures in Table 3 are obtained; for convenience these are expressed relative to the blank (A) mix as 100, and in increasing order.

Judging by the mean figures, none of the manganese compounds had a very marked effect, the worst being manganese dioxide, which gave 30 per cent more rapid deterioration than the blank, and even on the least favorable estimate this is only increased to 60 per cent.

The rate of deterioration bears no obvious relation to the nature of the manganese compound. Thus, the two forms of the dioxide (mixes L and F) are at opposite ends of the list, as are also the two water-soluble salts (G and B). The natural minerals (K, L, M, N, P) are scattered through the list, and thus do not appear to be either more or less active than the average.

The investigation was extended by studying two further series of mixes, designed to examine (1) the effects of a high proportion of acidic softener, which might be expected to form rubber-soluble, and hence presumably more active, manganese compounds; and (2) the effects of manganese salts of organic acids.

The experimental details were generally as described above, except that blanc fixe was used in place of barytes as the filler, and in Series (1) two base mixes were used, containing, respectively, 4 parts of stearic acid and 4 parts of naphthenic acid in place of the 1 part of stearic acid previously used. Manganous chloride and sulfate, manganese dioxide, and pyrolusite were tested in each of these mixes; the first two compounds were dissolved in water and mixed with the filler with the object of still further improving dispersion, since it seemed possible that their inertness in the previous tests was due to inadequate dispersion.

In Series (2) the following manganous salts were tested: formate, lactate, citrate, stearate, oleate, linoleate, naphthenate, and resinate; an additional inorganic salt (manganous borate), not previously examined, was included. These were tested in the base mix containing 4 parts of stearic acid.

Results were obtained up to 56 days in the Geer oven and 192 hours in the bomb. Table 4 shows the tensile strength for the blank mix and the range of

TABLE 4

TENSILE STRENGTH (LBS. PER SQ. IN.)

Softener		Unaged	14 days in oven	56 days in oven	96 hours in bomb	192 hours in bomb
Stearic acid	Blank mix	3450	2750	1000	2500	1825
	Series (1)	3100–3675	2425–2825	925–1550	2050–2450	1100–1925
	Series (2)	3225–3675	2300–2800	850–1650	2300–2600	525–1975
Naphthenic acid	Blank mix	3450	2425	650	1625	—
	Series (1)	3075–3750	1975–2275	550–825	1250–1650	—

values in each series containing manganese compounds.

In Series (1) the only rubber showing definite signs of worse aging than the blank is that containing pyrolusite and stearic acid, and even here the effect is shown only in the 192-hour bomb test (1,100 lbs. per sq. in., compared to 1,825 lbs. per sq. in. for the blank). Even in the presence of a considerable proportion of acidic softener, therefore, the inorganic manganese compounds did not cause serious deterioration.

The same conclusion applies to Series (2), although a few of the compounds, such as the lactate, stearate, and oleate, do appear to have noticeably accelerated the deterioration, especially in the 192-hour bomb test (525–1,000 lbs. per sq. in. tensile strength).

All the naphthenic acid mixes deteriorated more than the corresponding stearic acid mixes. As this is almost, if not quite, as evident in the blank as in the manganese-containing mixes, it is clearly a direct effect of the naphthenic acid rather than an activation of the manganese. Previous work has indicated that naphthenic acid may have an adverse effect on aging.

SUMMARY

1. Information received from rubber manufacturers on their experience of the effects of manganese and copper on aging is summarized. Although there is evidence that the amounts of these impurities in fillers tended to increase during the early war years (1939–42), it seems to be the general experience that little trouble arose from their effects on the properties of the rubber. Fillers containing as much as 0.05–0.10 per cent of manganese, or 0.005 per cent of copper, have not shown any obvious harmful effects.

2. Experiments with a large number of manganese compounds, including naturally occurring (mineral) forms and salts of organic acids, used in amounts equivalent to 0.01 per cent manganese on the raw rubber, have failed to show any pronounced harmful effect on the aging (oven or oxygen bomb) of a vulcanized natural rubber containing mercaptobenzothiazole, although deterioration was noticeably accelerated in some cases. Probably on account of the smallness of the effects observed, it is not possible as yet to draw any conclusion as to the relative activities of different types of manganese compound.

3. According to results of previous workers[12], manganese in the amount used in the present experiments can produce a more serious effect than these experiments indicate. The effect of manganese is known to depend on the type of mix used[6], and this aspect of the problem would thus appear to merit further investigation, as does also the influence of the method and degree of dispersion of the manganese compound in the rubber mix.

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HYSTERESIS AND METHODS FOR ITS MEAS-
UREMENT IN RUBBERLIKE MATERIALS *

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NATURE OF HYSTERESIS AND SIGNIFICANCE OF VARIOUS HYSTERESIS EXPRESSIONS

After a piece of rubber undergoes a mechanical distortion, it is never the same again. The truth of this statement depends, of course, on the degree of precision and discrimination of the observations. Superficially, and for most most practical purposes, it may appear to be unaltered. The point is that in any deformation of rubber there are always some irreversible processes which lead to the conversion of mechanical energy into heat and to a departure from the behavior of an ideal elastic material.

Tests which have been used to evaluate hysteresis loss in rubberlike materials may be classified as follows:

1. Low-speed stress-strain loop.
2. Impact resilience.
3. Free vibration.
4. Forced vibration at resonance.
5. Forced vibration; nonresonance.

We shall first discuss the general principles involved in these different methods of testing and then will describe the experimental procedures and results in more detail.

For relatively large, slow deformations, depending on the experimental conditions, imperfections in elasticity become evident as hysteresis, permanent set, creep, time lag for recovery or stress relaxation.

LOW-SPEED STRESS-STRAIN LOOP

The familiar tension hysteresis loop is shown in Figure 1. The area of the loop is proportional to the elastic energy which has been converted into heat. The total work expended on the rubber is the area under the curve ABC. Hence the percentage hysteresis or hysteresis loss is defined as the ratio of the area of the loop to the area under the curve ABC expressed in percentage.

From inspection of the loop it becomes evident that its occurrence can be

ascribed either to creep, stress relaxation, or time lag of recovery, depending on the point of view. Likewise, the permanent set, AE, contributes to the hysteresis.

For small, rapidly repeated deformations the hysteresis loss becomes readily observable as a temperature rise in the test-piece. All these phenomena, hysteresis, set, creep, stress relaxation, and heat development on flexing are the external manifestations, in whole or in part, of fundamental molecular processes which occur when the rubber structure accommodates itself to stress. Segments of the long-chain molecules in any localized region have preferred orientations or configurations with respect to each other. The application of stress disturbs these configurations and requires new equilibrium configurations. For some types of rubber this molecular readjustment may actually result in crystallization or a fixation of the molecules in a space lattice. In the process of passing from the unstressed to the stressed configurations some of the applied
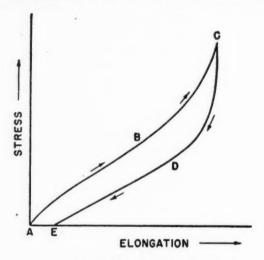
Fig. 1.—Static hysteresis loop.

mechanical energy is degraded by molecular vibrations and rotations and energy losses occur.

Mechanical models to represent the elastic behavior of rubber have been frequently proposed[1]. They consist of springs with dash-pots as friction elements. The mathematical procedures for solving such systems are definite and straightforward[2]. Four such models are shown in Figure 2. Model A is a simple model, consisting of a spring and dash-pot in parallel. It suffices to describe many of the vibration phenomena with rubber. Model B is the series model employed by Maxwell in his theory of relaxation phenomena. If it is desired to explain the elastic behavior of rubber in more detail by such models and to include a wider range of elastic phenomena, it becomes necessary to introduce more elements into the model thus increasing its complexity. Model C represents one step in this direction; the series elements help to explain long-term creep and stress relaxation. The most general system of this type consists in a parallel network of Maxwell elements (dash-pot and spring in series), shown in Model D.

A. Parallel model.

B. Maxwell model.

C. Model with series creep element.

D. Generalized model.

Fig. 2.—Mechanical models.

Such models can be readily devised to explain a limited range of phenomena, but in doing this explaining, care must be taken to avoid inconsistencies with other data equally as significant. These models are to be regarded merely as formal aids to thinking at the present time, although eventually it may be possible to identify various aspects of the molecular structure with the different elements.

IMPACT RESILIENCE

Probably the most widely used test for estimating the resilience of rubber is the ball or pendulum rebound test. In this test the percentage of the original impact energy which is returned to a ball or pendulum after impact with a block of rubber is determined. It is not a vibration test which is characterized by a cyclic interchange of potential and kinetic energy, but workers using vibration tests have usually tried to correlate their results with the rebound test and to interpret them in terms of rebound. This practice has led to some confusion and error, and it explains many of the forced interpretations of vibration results. The closest analogy which can be drawn between the rebound test and a vibration test is to regard the deformation in the rebound test as corresponding to a half cycle of damped vibration.

For free vibrations, where a mass is supported by rubber and set into oscillation at the natural frequency of the system, hysteresis becomes evident as a falling off or decay of amplitude for successive vibrations.

The equation of motion is:

$$m \frac{d^2x}{dt^2} + b \frac{dx}{dt} + sx = 0 \tag{1}$$

with the solution:

$$x = x_0 e^{-bt/2m} \cos p_0 t \tag{2}$$

$$p_0 = \frac{\sqrt{4ms - b^2}}{2m} \tag{3}$$

For critical damping:

$$b_c = 2m \sqrt{\frac{s}{m}}$$

m = mass (grams)
x = displacement (cm.)
t = time (sec.)
b = constant of proportionality between frictional force and velocity (dynes per cm. per sec.)
s = spring stiffness (dynes per cm.)
p_0 = angular frequency (radians per sec.).

Figure 3 shows a damped free vibration as given by Equation (2).

Resilience is defined in the dictionary in its engineering usage as the energy given back by a body which is released after being strained up to its elastic limit or, alternatively, the energy required to stress a body to its elastic limit. In the application of the word to rubber, it has been used in a very broad sense and with various shades of meaning. Since rubber does not have an elastic limit in the ordinary sense, some modification of the definition is required if the word is to be used at all in connection with rubber. The term "proof resilience" has been used to denote the energy required to stress a cubic inch of rubber to its breaking point. But the term "resilience" in connection with rubber has

acquired a general significance as expressing the relative amount of energy which is returned by the rubber after any deformation.

FREE VIBRATION

For a rubber vibration test, it seemed advisable to qualify the word and to extend its usefulness by defining the "dynamic resilience" as the fraction of the vibrational energy which persists in the second of two successive free vibrations. The damping, or the fraction of the vibrational energy dissipated as heat in a cycle of vibration, is then (1 − dynamic resilience).
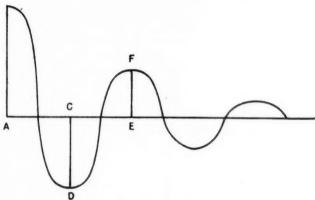
Fig. 3.—Free vibration.

The energy in a vibration is proportional to the square of the amplitude. Therefore, referring to Figure 3:

$$\text{Dynamic resilience} = \overline{EF}^2/\overline{AB}^2 = R \qquad (4)$$

From Equation 2, by letting t equal the periodic time, $2\pi/p_0$, it follows that:

$$\frac{\overline{EF}}{\overline{AB}} = e^{-\pi b/m p_0} \qquad (5)$$

and

$$R = \frac{\overline{EF}^2}{\overline{AB}^2} = e^{-2\pi b/m p_0} = e^{-2\pi p_0 b/s} \qquad (6)$$

The logarithmic decrement is

$$\ln \frac{\overline{AB}}{\overline{EF}} = \frac{\pi b}{m p_0}$$

To secure values of resilience which corresponded to those with the rebound pendulum, Naunton and Waring[3] used the ratio, $100\ EF/AB$, as the resilience. This is the percentage of the vibrational energy which remains after half a cycle of vibration.

Yerzley[4] called $\dfrac{\overline{EF} + \overline{CD}}{\overline{AB} + \overline{CD}}$ the percentage resilience. This ratio can be shown to be equivalent to $\sqrt{\overline{EF}/\overline{AB}}$ or the fourth root of the dynamic resilience[5].

The most practical interest attaches to the energy losses which occur in the case of rapidly repeated, relatively small deformations because in this case the heat developed may become destructive.

For forced or sustained vibrations with a sinusoidal driving force $F \cos pt$, the equation of motion is:

$$m \frac{d^2x}{dt^2} + b \frac{dx}{dt} + sx = F \cos pt \qquad (7)$$

The steady state solution of which is:

$$x = \frac{F}{\sqrt{(s - mp^2)^2 + b^2 p^2}} \cos (pt - \phi) \qquad (8)$$

where the phase angle is:

$$\phi = \tan^{-1} \left(\frac{bp}{s - mp^2} \right) \qquad (8a)$$
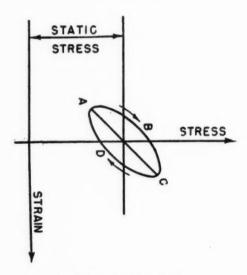
Fig. 4.—Vibrational hysteresis loop.

The presence of the damping term $b \frac{dx}{dt}$ results in the dynamic stress-strain cycle shown in Figure 4. The hysteresis loop is an ellipse, and its area represents the energy dissipated per cycle.

FORCED VIBRATION AT RESONANCE AND NON-RESONANCE

Laboratory tests employing forced vibrations of a rubber-mass system tuned to resonance[6] have proved to be very useful in evaluating hysteresis losses. Here the effect of the damping is to limit the amplitude at resonance to a finite value.

From Equation 8, at resonance ($x = x_{\max}$), so:

$$p^2 = \frac{s}{m} - \left(\frac{b}{2m}\right)^2$$

or to a first approximation:

$$s = mp_0^2 \tag{9}$$

$$b = \frac{F}{p_0 x_{\max}} \tag{10}$$

Consequently s and b can be determined by measurement of the amplitude, frequency, mass, and driving force at resonance.

It has been found experimentally that the product bp is approximately constant as frequency is varied. s is also invariant with frequency. Hence both the amplitude at resonance [see Equation (10)] and the dynamic resilience as given by Equation (6) are insensitive to frequency.

Kosten[7] made use of the invariance of bp with frequency to express the results of vibration tests in terms of the close analogy which exists between oscillating electrical circuits and vibrating mechanical systems. Analogous to the angle of loss in alternating current theory, he defined the angle of loss for rubber as δ where

$$\tan \delta = \frac{bp_0}{s} \tag{11}$$

For rubber test-pieces vibrating in compression, s and b are dependent on the size and shape, except for very low shape factors[8]. The shape factor is the ratio of the loaded area to the free area of the test-piece. Independence of size can be secure by defining new quantities, E and η, given by:

$$E = s\left(\frac{h}{A}\right) = s.q. \tag{12}$$

E = dynamic modulus
h = height of test place
A = area of test piece
q = form factor

$$\eta = \left(\frac{h}{A}\right) = b.q. \tag{13}$$

η is called the internal friction. It has dimensions of viscosity in the case of shear vibrations.

In these terms,

$$R = e^{-2\pi p_0 \eta / E} \tag{14}$$

For shear vibrations, the equations are essentially the same. In this case use of the factor h/A gives values for η and G, the shear modulus, which are independent not only of size, but also of the shape of the test-piece. This point has been established by Dillon, Prettyman, and Hall[9].

The heat generated per cycle of vibration can be calculated by performing the integration $\int bX dx$ over a complete cycle. The result is:

$$H_x = \frac{\pi p \eta X^2}{q} \tag{15}$$

or

$$H_F = \frac{\pi q p \eta F^2}{(E - mqp^2)^2 + \eta^2 p^2} \tag{16}$$

where X is the amplitude of vibration, and F is the maximum value of the impressed force. H_x is the heat generated per cycle for constant amplitude vibrations. H_F is analytically equal to H_x, but is in a form convenient for calculating the heat generated per cycle in constant force vibrations. The expressions are both general and apply to the vibrations in the testing apparatus or to a product subjected to a periodic impressed force. For the case of a tire, where the operating frequency p is generally much below the resonance frequency $p_0 = \sqrt{E/mq}$, we then have:

$$H_x = \frac{\pi p \eta X^2}{q} \tag{17}$$

$$H_F = \frac{\pi q p \eta F^2}{E^2} \tag{18}$$

Now for small values of $p\eta/E$:

$$R = e^{-2\pi p\eta/E} = 1 - 2\pi p\eta/E$$

or

$$\pi p \eta \approx \frac{E}{2}(1 - R)$$

Thus we obtain H_x and H_F in terms of the dynamic resilience R as:

$$H_x \approx \frac{1}{2q}(1 - R)EX^2 \tag{19}$$

$$H_F \approx \frac{q}{2}(1 - R)\frac{F^2}{E} \tag{20}$$

For constant amplitude vibrations, the relative heat generation at a given frequency of two stocks 1 and 2 can be calculated from the ratio η_1/η_2 or $(1 - R_1)E_1/(1 - R_2)E_2$. Likewise the relative heat generation at constant impressed force is given by $\eta_1 E_2^2/\eta_2 E_1^2$ or $(1 - R_1)E_2/(1 - R_2)E_1$.

The determination of the relative values of H_x and H_F is the important accomplishment of forced vibration testing.

Direct determinations of heat generation in rubber can be made by observation of the temperature rise in a rapidly flexed test-piece. Here there is the advantage that in such a comparison the various rubber samples run at different temperatures built up by flexing, as is the case in service. A number of flexometers have been developed for such measurements[10] but they have suffered in general from the disadvantage that they do not employ well-defined static and dynamic strain and stress conditions.

APPLICATION OF HYSTERESIS MEASUREMENTS

The diversity of methods for determining hysteresis losses requires that careful consideration be given to the significance of any particular laboratory result for a given application. Where a choice of methods is available, it is, of course, highly desirable to select the one which approximates service conditions most closely with respect to such variables as frequency, amplitude, temperature, etc.

One of the most important points involves the question as to whether the stocks to be compared work with the same deformation or whether the deformation depends on the stiffness of the stock. As indicated by Equations (19) and (20), the relative ratings of two stocks with respect to heat generation may

easily be reversed, depending on whether they are compared under constant amplitude or constant force conditions. If in service the deformation of the stocks is not the same, but varies owing to the stiffness of the stock, then the dynamic modulus as well as the hysteresis loss must be taken into account in estimating the heat generation and in evaluating test results.

Clear-cut illustrations of constant force and constant amplitude applications are offered by solid tires and rubber belts, respectively. In the case of a pneumatic tire tread, the deformations occur under a complicated set of circumstances, some elements of which correspond to constant force and some to constant amplitude conditions.

In selecting the type of hysteresis test which seems most desirable for tread stocks, it is well to consider the frequency and amplitude involved. The speed of deformation for normal operating conditions corresponds to a frequency of the order of several hundred cycles per second. This is estimated from the time interval involved in the load application to a small, finite element of length of the tread, such as, for instance, a button in the tread design. There is, of course, an interval of rest between load applications so that the actual deformation history would probably require a Fourier analysis for a mathematical description. Nevertheless it is apparent that a laboratory test for hysteresis in this case should be carried out at relatively high frequencies and low amplitudes.

Resiliometer (drum) tests carried out to investigate the mechanism of heat generation in tire treads[11] indicate that approximately 50 per cent of the temperature rise could be attributed to amplitude cycles of magnitude independent of the stiffness of the stock; the other 50 per cent is due to force cycles the deformations from which would depend on the stiffness.

This situation requires a laboratory test which evaluates stocks under both constant force and constant amplitude conditions. A forced vibration test appears to be the most desirable of any proposed, both with respect to approaching the service conditions and in its ability to give the information wanted.

Of the forced vibration tests, a flexometer test is the most direct, but means must be provided for measuring the temperature rise under both constant force and constant amplitude conditions.

REVIEW OF VARIOUS HYSTERESIS TEST METHODS

The foregoing discussion has set forth in a rather general manner the nature of hysteresis from the viewpoints of both gross mechanical systems and idealized molecular models. The significance of the various types of hysteresis indices with respect to service conditions has also been treated. A detailed review of the five principal classes of hysteresis tests will follow.

LOW-SPEED STRESS-STRAIN HYSTERESIS LOOP METHOD

Measurement of the area between the extension and retraction curves, as obtained with various types of tensile testers, was probably the earliest form of hysteresis test. It was soon found that the area of the hysteresis loop rapidly decreased in successive cycles of extension and retraction, reaching an approximately constant minimum value (equilibrium value) in the fourth or fifth cycle[12]. The area of the loop decreases markedly, with increasing temperature[13].

In general, the hysteresis loss per cycle has been expressed as the area of the loop divided by the area between the extension curve and strain axis, i.e., the fraction of the energy of extension absorbed by the rubber sample per cycle.

This hysteresis index, which we shall call H_1, is easily measured either in tension or compression and is clear-cut in interpretation, provided it is remembered that it refers to a particular arbitrary set of testing conditions. Unfortunately H_1 varies with the rate of strain, minimum strain and previous strain history in a rather complicated manner[14]. Since rubber seldom finds application under the conditions of strain and rate of strain found in an ordinary tensile machine, it is very dangerous to rely on the static hysteresis as a fundamental indication of the hysteresis defect of a given polymer or stock. A study of hysteresis loops for GR-S in comparison with *Hevea* does show significant differences in dependence on strain[15].

IMPACT HYSTERESIS METHOD

Another type of hysteresis test which has been employed since the beginning of rubber technology is the impact resilience test[16]. Impact resilience is defined as the returned fraction of the available impact energy of a freely falling fall or pendulum hammer, striking and rebounding from a rubber block. Thus, if y_0 is the vertical height of fall of a ball or pendulum hammer, and y_1 is the height of rebound, impact resilience is y_1/y_0. The fractional impact hysteresis loss is then $H_2 = 1 - y_1/y_0$.

Both simple and compound pendulums have been employed. One simple form of impact resilience apparatus consists of a steel ball bearing, released from one pole of an electromagnet so that it falls upon the flat horizontal surface of a rubber block held against a heavy steel plate by vacuum applied through small drilled holes in the plate[9]. The percentage resilience is read directly on a vertical scale. When only small polymer samples are available, the apparatus may be operated by dropping small cured rubber balls (0.5-inch diameter or smaller) against a steel plate and noting the rebound. The rubber balls are released by destroying a vacuum in a small hole drilled axially in the electromagnet core. It has been found that excellent correlation exists between the results of the various impact resilience tests although the absolute magnitude of the resilience depends on ball (or hammer) size[17] and shape and to a small extent upon the effective height of fall (see Table 1).

TABLE 1

BALL REBOUND *vs.* BALL SIZE AND HEIGHT OF FALL

	Room temperature (Cm.)				
Height of fall	61	81	100	100	100
Steel ball diameter	1.9	1.9	1.9	1.27	0.8
	Percentage ball rebound				
Stock					
Hevea gum	82.0	81.0	80.5	75.5	61.0
Hevea tread	57.4	57.4	56.8	54.0	46.0
GR-S gum	53.3	52.5	52.0	49.0	40.0
GR-S tread	31.2	31.5	30.5	29.0	28.0

	Cm.		
Height of fall	100	100	100
Rubber ball diameter	2.54	1.27	0.63
	Percentage ball rebound		
Stock			
GR-S tread	47.0	46.0	40.0

Windage is generally a small factor, but care must be taken to hold the rubber block tightly against a heavy mass. Pendulum supports should be very rigid. As in the case of all hysteresis tests, hysteresis decreases (rebound increases) on successive impacts, but reaches a stable value after three or four impacts. Some workers recommend a vigorous beating or repeated deformation of the sample before testing to attain equilibrium, but this is generally unnecessary; repeated impacts of the ball or hammer at the same point on the sample generally give a simpler and more reproducible pretreatment.

Tests at elevated temperatures are easily performed with impact tests, since the resilience is altered very little by the stiffer surface layers of the sample which result from cooling immediately after removal from an oven. Five or six repeat rebounds can easily be obtained with the falling steel ball apparatus, described above, when the rubber cylinders (0.75-inch high, 1.59-inch diameter) are heated to a uniform temperature of 100° C, quickly removed from the oven, and placed on the vacuum platen. Seriously misleading results are obtained, however, if the sample is allowed to cool, and rebounds are taken at successively lower temperatures, as indicated by a thermocouple with junction imbedded in the sample[18]. The temperature distribution within the sample changes with time, and the temperature of the outer layers of rubber becomes increasingly a controlling factor as the sample cools.

Hence, if the thermocouple junction is in the center of the sample, it indicates too high a temperature in the intermediate stages of cooling. If the junction is near the surface of the sample, it indicates too low a temperature in the earlier stages. Obviously the correct procedure is to preheat the samples in an oven set at the desired temperature of test and transfer them and test them as quickly as possible. The use of a thermocouple is unnecessary except to indicate attainment of the oven temperature at the center of the sample. It should be remarked that greater care must be taken with tests at low temperatures, since the softer warming surface layers of the sample affects appreciably the rebound within less than a minute after removal of the samples from the cold chamber. Condensed moisture on the samples undoubtedly affects the results, but reliable data can be obtained by rapid manipulation.

The impact resilience type of test is extremely simple, rapid, and precise, and it is not surprising that it has come into almost universal use in the development of synthetic polymers. Unfortunately impact resilience is a function not only of the internal friction η, but also depends on the dynamic modulus E. For example, consider the case of a metal cylinder of mass, M, falling axially from a height, h_1, upon the flat surface, A, of a cylindrical rubber block of height, y. If h_2 is the height of rebound, and $h_2 > y$, the impact resilience may be calculated for the half cycle as:

$$R = \frac{h_2}{h_1} = e^{-\pi \eta / \sqrt{qME}} \tag{21}$$

where $q = y/A$. It is seen that R depends principally on the internal friction or hysteresis defect η, but also varies with the dynamic modulus E. In the large majority of cases η is the controlling factor in the exponent, but sometimes radical changes in polymer structure or compounding produce much larger changes in E than in η, and an increase in the value of R indicates an increase in modulus or hardness rather than a lower internal friction. Now η is the controlling factor in heat development in constant amplitude forced vibrations at a given frequency and, by definition, represents the hysteresis defect.

It thus appears extremely unfortunate that so much reliance has been placed on impact resilience which is a function of both η and E. Resilience is extremely easy to measure, of course, and is only slightly dependent on frequency, but these advantages hardly justify its use as a fundamental hysteresis index. In any event hardness (or better, dynamic modulus) must be taken into account when interpreting impact resilience data in terms of heat generation. The pendulum type of impact tester[19] offers definite advantages in this respect since relative values of dynamic modulus may be estimated from the "dynamic penetration", although the relation between modulus and penetration is not linear. Hence penetration values or their reciprocals cannot be used directly as a measure of dynamic modulus.

FREE VIBRATION METHOD

The free vibration method of measuring hysteresis has found considerable favor[20]. The most common technique employs a simple torsion pendulum system. The rubber sample is twisted to a fixed torsional deflection and released, thus going into damped torsional vibration, the radian frequency of which is approximately:

$$p_0 = \sqrt{\frac{G}{Iq^1}} \tag{22}$$

where G is the dynamic shear modulus, I the moment of inertia, and q^1 a geometrical factor which is constant for any particular rubber sample. The angular amplitudes for successive full cycles are then θ_1, θ_2, θ_3, and the resilience is calculated as:

$$R' = \left(\frac{\theta_2}{\theta_1}\right)^2 = \left(\frac{\theta_3}{\theta_2}\right)^2 = \ldots = e^{-2\pi p_0 \eta/G} = e^{-2\pi \eta/\sqrt{q'IG}} \tag{23}$$

This quantity is analogous to the impact resilience R except that it is calculated for a full cycle. It is nearly independent of the frequency selected, as are the variables $p_0\eta$ and G, in the frequency ranges usually employed. The same criticisms given for impact resilience apply to R', but it is possible to obtain G from the measured natural radian frequency p_0 and η can be calculated from the approximate relation:

$$\eta = \frac{q'Ip_0}{\pi} \ln \frac{\theta_n}{\theta_n + 1} \tag{24}$$

The possibility of measuring both η and G by the free vibration method gives definite advantage over the impact resilience technique. However, the method is by no means simple, since an accurate autographic recording of successive amplitudes is usually necessary and, in general, the natural frequency is not the same for different stocks, depending on the dynamic modulus G. Since values of η have absolutely no meaning unless comparisons are made at the same frequency and, since the empirical relationship $p_0\eta = \text{const.}$, found for forced vibrations at higher frequencies, is by no means well established in the low frequency range of free vibrations, interpretation of values of η obtained in free vibration is difficult. Furthermore the range of damped amplitudes observed with a single type of free vibration test is rather large, and the variation of η and G with amplitude often introduces serious error. In general, it may be said that reasonably accurate results can be obtained by the free vibration method when η is reasonably small, but with η large, as in the case of GR-S type polymers, results are erratic and misleading.

FORCED VIBRATION.   RESONANCE METHODS

The resonance method is performed with apparatus which is essentially a mechanical circuit consisting of the rubber sample of stiffness s, a mass M, and a periodic impressed force, $F \cos pt$.   The circuit is tuned to resonance by varying either the mass or the impressed frequency so that $s \approx Mp_0^2$, where p_0 is the natural radian frequency.   The resonance amplitude is $X_0 = F/p_0b$, where b is the coefficient of the velocity term in the differential equation (see Equation 7). s is related to the dynamic modulus, and b to the internal friction by a constant of proportionality q, which depends on the geometry of the system. The sinusoidal impressed force may be either mechanical or electrical.

An example of a mechanically driven resonance vibrator is that of Kosten[21], which is illustrated in Figure 5.   The apparatus was driven by "off-axis" masses m which were rotated at radian frequency p.   There actually were pairs of such masses, rotated in opposite senses to eliminate horizontal forces.   The vertical centrifugal driving force (compressional) was then $4mp^2r \cos pt$, where r was the off-axis distance of the masses m.   The samples could be compressed by means of a stiff spring the force of which, added to the mass M, constituted the constant static load.   The system could be tuned to resonance by varying
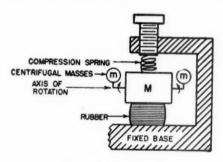
FIG. 5.—Kosten apparatus.

the mass M or altering the driving frequency.   Kosten employed the angle of loss δ defined by $\tan \delta = p_0b/s = p_0\eta/E$.   He found that $p_0\eta$ and E were nearly independent of frequency, and thus δ is independent of frequency and is analogous to the angle of loss employed in electrical measurements.

This type of apparatus has also been employed by Gehman[8] in a comprehensive study of the effect of "shape factor" on η and E.   The method is effective for the study of large rubber samples or complete assembled vibration dampers.   The fact that the centrifugal driving force increases with frequency is a distinct disadvantage when attempting to make measurements at either constant force or constant amplitude.   The method is thus not suitable for hysteresis evaluation of synthetic polymers.   Fletcher and Schofield[22] have used the method to investigate the dependence of dynamic properties of synthetic rubbers on temperature.   An interesting illustration of its usefulness in an engineering application of rubber is described by Zdanowich and Moyal[23] in connection with the development of rubber dampers for the suppression of torsional vibrations.

The first published method which employed electrically-forced vibrations was that of Naunton and Waring[3].   Their apparatus (Figure 6) was driven by the output of a vacuum tube oscillator which was connected to a coil attached

to a mass M. The coil was located between the poles of a permanent magnet. Oscillations of the mass M caused the two statically compressed rubber samples to execute compressional vibrations about the static compression. The static compression was regulated to give a static stress of 2 kg. per sq. cm. The dynamic amplitude was measured with an electromagnetic pickup. Measurements of η and E were made over a wide range of frequencies (80 to 500 cycles per second). Unfortunately the driving mechanism was attached rigidly to a heavy base plate "to avoid great transmission of vibration". This practice, of course, resulted in exactly the opposite condition; appreciable energy was transmitted to the supports. This condition may explain some of the erroneous results obtained: increase of E with frequency, maxima in the resilience vs. frequency curves, etc.
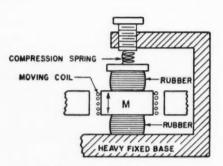
Fig. 6.—Naunton and Waring apparatus.

The Goodyear resonance vibrator[24] constitutes a considerable improvement over that of Naunton and Waring (see Figures 7 and 8). As in the case of Naunton and Waring's apparatus, compressional vibrations are used, but the equilibrium position is one of constant static deflection rather than constant static load. Amplitudes are measured directly by means of a traveling microscope or projected on to a ground-glass screen. The whole system is mounted on a sponge rubber pad which effectively prevents appreciable energy loss to the table. The driving power is taken from the 60 cycle per second mains through an autotransformer or from a variable frequency oscillator. The impressed force is measured by the current through the coil; the force vs. current relation is determined by calibration with direct current. Thus the static modulus
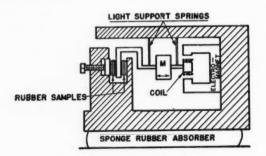
Fig. 7.—Goodyear resonance vibrator.

E_{st} can also be measured with direct current. The system is usually tuned to resonance at 60 cycles per second by varying the mass M, and E and η are calculated from the resonance conditions; $E = Mqp_0^2$ and $\eta = qF/p_0X_0$. It is also possible to calculate the dynamic resilience, $R = e^{-2\pi p_0\eta/E}$, as well as the heat generation per cycle to be expected in rubber products[25]:

$$H = \frac{\pi p \eta X^2}{q} = \frac{\pi q p \eta F^2}{(E - Mqp^2)^2 + p^2\eta^2} \tag{17a}$$
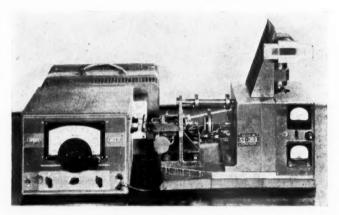
Fig. 8.—Goodyear resonance vibrator.

Gehman, Woodford and Stambaugh[26] showed with this apparatus that the variables ηp_0 and E are nearly independent of frequency, in agreement with the results of Kosten[7]. The values of η and E depend on the shape of the test-piece and the static deflection in the manner to be expected from static deflection experiments[27]. Both η and E decrease with increasing amplitude, but, by making measurements at approximately the same amplitude and the same frequency, very precise measurements may be made, which give reliable relative values of the hysteresis defect η for various stocks, especially when measurements are made at elevated temperatures[28].

The Firestone resonance vibrator[9] is similar to the Goodyear apparatus except that the rubber samples are vibrated in simple shear (see Figures 9 and 10). The samples are subjected to a 15 per cent static compression at right
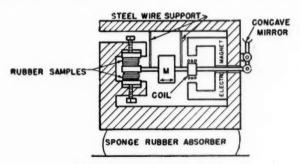
Fig. 9.—Firestone resonance vibrator.

Fig. 10.—Firestone resonance vibrator.

angles to the shear motion.   The amplitude is measured by means of an optical lever.   The light from a fixed source is reflected from a moving concave mirror to form an illuminated line on a transparent scale.   When a direct current is passed through the coil, the movement of a spot of light on the scale gives the static deflection and allows calculation of the static shear modulus G_{st}.   The rubber samples are enclosed in a small air oven, the temperature of which is controlled for half the control cycle of a recorder-controller by means of a small thermocouple junction located at the center of one of the rubber samples, with wires in a single plane parallel to the shear stress.   The other half of the control cycle responds to another thermocouple junction just outside the rubber sample. Thus measurements above room temperature are made with nearly constant temperature throughout the rubber samples.   Measurements below room temperature are made by passing expanding carbon dioxide gas into the oven. As in the case of the Goodyear apparatus, stock comparisons are usually made under the resonance condition at 60 cycles per second, attained by varying the mass M, but a variable frequency oscillator is available for studying the frequency dependence of η and G which are defined by the differential equation[29]:

$$\frac{y}{A} M \frac{d^2e}{dt^2} + \eta \frac{de}{dt} + Ge = \sigma \cdot \cos pt \tag{7a}$$

where σ is the maximum shear stress per sample, e is the instantaneous shear strain, A the shear area, and y the thickness of the sample.   The solution gives the maximum shear strain as:

$$e_{max} = \frac{\sigma}{\left(G - \frac{y}{A} M p^2 \right)^2 + p^2 \eta^2} \tag{26}$$

or at resonance:

$$e_0 = \frac{\sigma}{p_0 \eta} \; ; G = \frac{y}{A} M p_0^2 \tag{27}$$

and the heat generation per cycle, per unit volume, is:

$$H\sigma' = \frac{\pi p \eta \sigma^2}{\left(G - \frac{y}{A} M p^2 \right)^2 + p^2 \eta^2} \; ; He' = \pi p \eta e^2_{max} \tag{28}$$

which becomes at resonance:

$$H_0' = \frac{\pi\sigma^2}{p_0\eta} = \pi p_0\eta e_0^2 \qquad (29)$$

It should be noted that G is the dynamic shear modulus, and η, the internal friction, which is defined as the viscosity of the test-piece, *i.e.*, η = viscous restoring stress/rate of shear. G and η decrease with increasing static compression (at right angles to shear stress), since the slope of the stress-strain curve decreases with increasing strain in the vicinity of the origin. However, G and η do not depend on either the size or shape of the samples, over a wide range, provided the static compression is maintained constant. This is an important advantage for the shear method since, by choosing several different sample shapes of a given stock, a wider range of resonance frequencies may be obtained, and very small samples may be employed without seriously reducing the amplitudes. In Figure 11 the variation of η with frequency is given, using
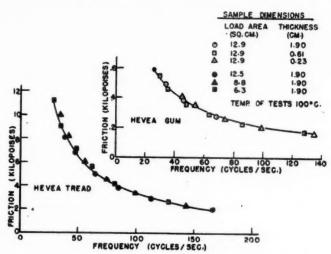
Fig. 11.—Internal friction *vs.* frequency with various sample shapes
(Firestone resonance vibrator).

radically different sample shapes. The ability to make precise measurements on samples as small as 0.5-gram (total stock required = one gram) is applied in evaluating experimental polymers where only a few grams of polymer are available for a complete set of physical tests.

The dependences of internal friction and modulus on frequency and temperature are very similar to those found with the Goodyear apparatus[26] (see Figures 12, 13). In agreement with Kosten[7] and Gehman, Woodford and Stambaugh[26], G and $p_0\eta$ are found to be only slightly dependent on frequency. However log-log plots of the type shown in Figure 14 indicate that $\eta = kp_0^{-n}$, where k and n are constants for a given stock at a given temperature. For tread and gum stocks based on a wide range of different polymers, n has been found to vary from 0.78 to 1.00.

Moyal and Fletcher[30] found that resilience values calculated from forced resonance amplitudes agreed satisfactorily with those calculated from the damping of free vibrations of the same system.

Vibration devices in which resonance is purposely avoided are generally termed flexometers in the rubber industry. In general, a flexometer operates under a more or less arbitrarily chosen set of conditions aimed at developing heat in a rubber sample, which can be measured as temperature rises.
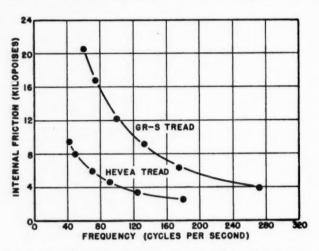
Fig. 12.—Internal friction *vs.* frequency-temperature of test 40° C, impressed periodic force 1,000 grams, thickness of test sample 0.75-inch.
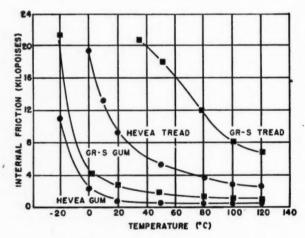
Fig. 13.—Internal friction *vs.* temperature (Firestone resonance vibrator).

FORCED VIBRATION. NON-RESONANCE METHODS

The ability to withstand "blowout" is also measured in some flexometers, but, since this involves chemical resistance of the stocks to heat as well as hysteresis losses, the blowout feature will not be discussed in this paper. Furthermore the permanent static deflection of the rubber sample after a definite cycle of testing is usually obtained, but, because of its indirect relation

to hysteresis, will not be considered here.   The temperature rise for given
sample size and shape under any controlled set of conditions depends to some
extent on the thermal conductivity and the rate of loss of heat to the surround-
ings by radiation and convection.   Fortunately the termal conductivity is very
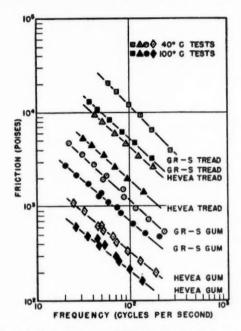
FIG. 14.—Log-log plots of η vs. frequency—GR-S and natural rubber gum and tread stocks.

nearly the same for the common rubberlike polymers; so, for a given sample
size and shape, the measured temperature rise is primarily a measure of the
hysteresis losses under the particular set of conditions employed.   The choice
of the conditions of static and dynamic stress and strain is, however, very
important and has been unfortunate in some cases.

The Firestone flexometer[31] has been of considerable value to rubber com-
pounders.   It is shown schematically in Figure 15.   A photograph of the
apparatus is shown in Figure 16.   A rubber sample approximately one inch
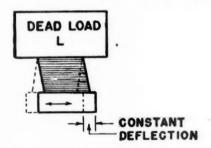
FIG. 15.—Firestone flexometer constant static load; constant shear amplitude;
temperature rise measured.

Fig. 16.—Firestone flexometer.

by two inches by $1\frac{1}{2}$ inches high is placed between Bakelite inserts in the top and the bottom platens. A vertical dead load, L, is applied, and the bottom platen is caused to rotate in a race in such a manner that the sample is subjected to a constant shear amplitude with continuously rotating shear axis. This motion is particularly convenient for routine testing, since it does not require accurate centering of the sample. As the test progresses, the temperature rises to an equilibrium value where the rate of heat generation is just balanced by the heat losses. The equilibrium temperature is measured with a needle thermocouple. As the temperature rises, however, the sample deforms to an increasing extent, so the condition is not strictly constant shear amplitude under constant vertical compressive load. If no permanent deformation takes place (a highly idealized condition) and if the initial sample height is y_1, the final height y_2, the constant throw x', then the change in height during the test is:

$$y_1 - y_2 = \frac{L}{A_1 E_{st}} \tag{30}$$

where E_{st} is the effective static modulus of compression at the equilibrium temperature, including the shape factor, and A_1 is the undeformed load area. If e_{max} is the maximum shear strain at the equilibrium temperature, then the constant throw is:

$$x' = e_{max} y_2 = e_{max} \left(y_1 - \frac{L}{A_1 E_{st}} \right) = \text{const.} \tag{31}$$

Thus the flexometer operates under a complex condition where neither the shear stress nor shear strain is constant. The common occurrence of permanent deformation during the test further complicates the conditions. Thus, only when the stocks to be compared have about the same value of E_{st}, does the machine give dependable relative values of the heat generation at constant

strain. The results are thus difficult to interpret in terms of the hysteresis defect. It should be pointed out, however, that the flexometer could be adapted to constant vertical deflection tests by clamping the top platen after loading the sample to a fixed deflection. In that case, essentially constant shear strain conditions would prevail. Preliminary trials, however, have shown that this technique results in horizontal motion of the specimens across the platens.
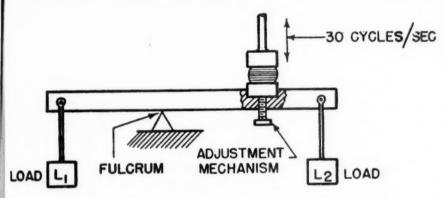
The Goodrich flexometer[32], like the Firestone flexometer, employs a constant amplitude and is mechanically driven. However the dynamic deflection is compressive. The compound load system (see Figure 17) is designed to have a low natural frequency of oscillation on the fulcrum. The position of the lower platen may be adjusted while the machine is operating so that the load arm remains approximately horizontal at all times and the compressional load is constant. As in the case of the Firestone flexometer, the sample generally assumes a permanent deflection in the course of the test. Thus, although the total load is constant, the static stress varies. Comparisons may be made either with constant initial compression or constant initial load. Equilibrium

FIG. 17.—Goodrich flexometer—constant static load or initial static deflection; constant compressive amplitude; temperature rise measured.

temperatures are measured with a thermal junction between the sample and the insulating platen insert or, in some cases, with the junction embedded in the sample. In the former case it should be noted that, since no heat is generated at the end of the sample by flexing, the thermocouple is heated by heat flow from the center, hardly a desirable situation. The machine is somewhat smaller than the Firestone flexometer and employs a smaller rubber sample (0.7-inch diameter by 1.0-inch height or smaller). Since neither the static stress nor static strain is constant during a test, unless the load is changed manually in proper proportion to the static deflection, complex conditions of test similar to those given for the Firestone flexometer exist (see Equation 31). The machine is equipped with an oven which permits tests at a controlled elevated ambient temperature.

The St. Joseph Lead Company flexometer[33] is considerably more versatile in regard to conditions of test than either the Firestone or Goodrich flexometers. The cylindrical rubber sample (see Figure 18) may be subjected to either constant vertical load or constant vertical deflection, but the first condition appears to be more generally used because of the tendency of the samples to

slip out of the machine under constant compression. The horizontal shear motion is produced by rotating the top and bottom platens about independent vertical axes which may be relatively displaced either by a constant horizontal load or a constant horizontal deflection. Thus it is possible to make equilibrium temperature measurements with constant static compressive strain with either constant horizontal shear strain or shear stress from which relative values of $H_{\epsilon'}$ or H_σ (see Equation 28) should be obtained by calculation from the relative temperature rises observed for various stocks.
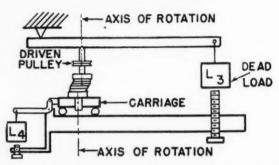
Fig. 18.—St. Joe flexometer—constant static load or deflection; constant shear load or amplitude; temperature rise measured.

Another type of nonresonance hysteresis testing device is the compressed rolling ball tester[34]. It consists of two parallel circular iron plates the upper one driven and the lower one stationary and having a V-shaped groove in which a 1.23-inch diameter solid rubber ball is rolled against the upper plate. The upper plate may be loaded or clamped to give a fixed deflection. The temperature of the ball is measured after a fixed time of running by means of a needle thermocouple. This apparatus appears to have good possibilities, particularly when the top plate is clamped. The difficulty of moulding uniform rubber balls must be admitted and also the fact that a continuous temperature record cannot be obtained.

Another well-developed type of nonresonance forced vibrator was that described by Roelig[35], which was extensively used in the German synthetic rubber development. This device, shown in Figure 19, consists of a mass M,
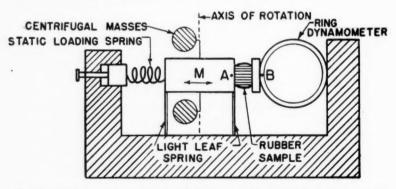
Fig. 19.—Roelig apparatus—constant static load; constant dynamic load—measures area of dynamic hysteresis loop by means of mirrors actuated by points A and B.

driven by centrifugal masses m, and forced against a rubber sample by means of a stiff compression spring to give constant static force. A mirror is actuated by point A on the mass M. Another mirror is actuated by Point B on the ring dynamometer. A beam of light is reflected from the two mirrors in such a manner that a dynamic hysteresis loop is traced on a screen. It should be noted that the force thus registered is the actual force on the rubber—not the driving force (termed $F \cos pt$ in this paper) on the system. Consequently the position of the loop is independent of the phase relation between the amplitude and the driving force. Thus the loop obtained with Roelig's apparatus is not the same as that shown in Figure 4, which rotates as the frequency is varied. Roelig defined the percentage damping as $100 \times$ area of the loop/triangular area under the loop. This procedure appears to base the loss per cycle on four times the vibrational energy in the cycle, so the damping values secured are about one-half as large as those from the rebound pendulum. Roelig's apparatus is very ingenious and is sound in principle when the damping is properly calculated. As a practical hysteresis test, however, it is somewhat cumbersome because of the necessity of measuring the area of the loop for each determination, an extremely laborious procedure.
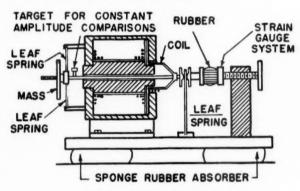
Fig. 20.—Goodyear flexometer.

The Goodyear flexometer is the most recently described non-resonance vibrator[11]. It is shown schematically in Figure 20. A photograph of the apparatus is given in Figure 21. The rubber sample (one- by one-inch by two-inches long) is compressed to 6 per cent between the fiber inserts of the platens by means of the adjustment screw operating against the stiff spring. Controlled 60-cycle current is supplied to the coil, which vibrates horizontally in a radial magnetic field. Since the central system of rod, coil, spring, and rubber sample is driven at 60 cycles per second, it is advantageous to have the natural frequency of the system in the vicinity of this value. This is accomplished by adjusting the mass M. This adjustment must be made only for stocks of greatly differing modulus. The sample is enclosed in a jacket, controlled at 35° C, during the test. The temperature at its center is measured by means of a needle thermocouple at the start of the test and after running for 10 minutes at fixed amplitude. The equilibrium temperature is not quite reached in 10 minutes, but the rate of change of temperature at that time is very small, so comparison of the 10-minute temperature rise for different stocks is significant. The amplitude is determined by visual observations of an arrow-shaped mark on the moving system through a magnifying lens or by an inertia

vibration pick-up. As the sample heats up, a few adjustments of the current are necessary to maintain the desired standard amplitude, but the system is stable and settles down rapidly. The temperature rise for a given stock is found to be approximately a linear function of amplitude X, indicating that the decrease of the internal friction η (see Equation 15) with temperature rise compensates partially for the X^2 factor in H_x.

Recently an attachment has been devised for the Goodyear flexometer which makes possible its adaptation for comparing the temperature rise in stocks flexed by the same alternating force. With this device the test-piece is loaded against a stiff spring which undergoes vibrations of very small amplitude. These are proportional in amplitude to the vibratory force on the rubber test-piece. The vibrations of the spring are amplified by means of a resistance strain gage and electronic amplifier. A steel spiral spring inserted in place of the rubber test block and vibrated at constant amplitude serves to calibrate the output of the amplifier. When the output is held the same for a series of stocks, a constant force comparison is secured.
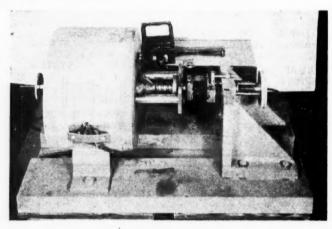
Fig. 21.—Goodyear flexometer.

Figure 22 illustrates the wide deviation between the constant force and constant amplitude comparisons for a series of GR-S stocks with different black loadings.

The Goodyear flexometer appears to furnish a straightforward method of measuring the hysteresis loss, either at constant amplitude or constant force, as demanded by the projected type of service for the stock tested. The measurement of temperature rise under properly controlled conditions removes much of the uncertainty caused by the temperature coefficients of η and G, when measured in a resonance-type forced vibrator with the object of calculating H_x and H_f. However, it is to be noted in Figures 13 and 26 that the temperature coefficients of η and G become rather small above 100° C, and, hence, if resonance comparisons are made of H_x and H_f within the range of operating temperatures, relative hysteresis figures are quite reliable. The somewhat undesirable characteristics of a compression vibration (shape factor and inability to obtain a continuous temperature record) are minimized in the Goodyear flexometer by the use of a long and narrow sample.
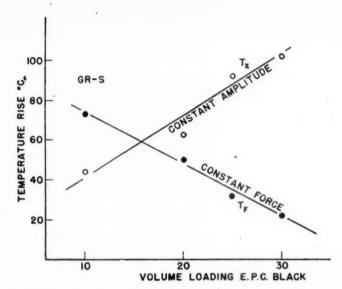
FIG. 22.—Goodyear flexometer comparison at constant amplitude and constant force.

COMPARISON OF RESULTS OF VARIOUS HYSTERESIS TESTS

It is hardly necessary to present data on static loop hysteresis measurements since this type of test has been found unsatisfactory and is now seldom used. However, representative compression hysteresis loops are shown in Figure 23. Since hysteresis is inherently a time effect, it is obvious that a static measure-
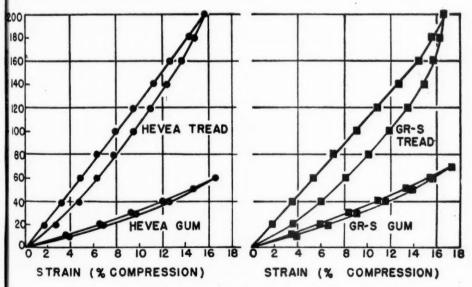
FIG. 23.—Compression stress-strain static hysteresis loops.

ment of it has little significance. Suffice it to quote an extreme case in the experience of one of the authors[36] where a stock (30 volumes black) based on an early Butyl type of polymer gave only 11 per cent hysteresis in an "equilibrium loading" loop, compared to 17 per cent for a control stock based on natural rubber. A rebound test showed only 7 per cent rebound, compared to 42 per cent for the natural rubber stock. These tests were made at room temperature. While this case is extreme and seldom experienced with other types of polymer, it indicates that the static stress-strain hysteresis loop can hardly be considered a dependable measure of the hysteresis defect.

A rather interesting comparison of ball rebound resilience and internal friction obtained by the forced vibration method is given in Table 2. A very good

TABLE 2

REBOUND VS. INTERNAL FRICTION

	Tests at 20° C			Tests at 120° C		
Stock type	Dynamic modulus (G)	Friction (η)	Rebound (%)	Dynamic modulus (G)	Friction (η)	Rebound (%)
Hevea gum	3.0	0.80	69	3.2	0.30	87
Tread	27.0	9.5	44	17.0	2.70	72
GR-S gum	4.8	2.80	57	4.0	1.00	73
Tread	60.00	30.00	37	17.0	6.8	50

NOTE: η Measured in Firestone shear vibrator @ 60 dycles per sec.; units; kilopoises.
G Measured in Firestone shear vibrator @ 60 cycles per sec.; units; megadynes per sq. cm.
% Rebound measured with falling ball (1.9 cm. diam.) from one-meter height.

correlation is shown for rebound and friction in comparing GR-S against *Hevea* in either gum or tread stocks. If attention is confined to a given stock, the temperature dependences of rebound and friction appear to be similar. However, if we compare the GR-S gum stock with the *Hevea* tread stock, we find that they give equal rebound at 120° C; whereas they differ greatly in the friction. This is an excellent example of the known dependence of rebound resilience on modulus. Another interesting example of the relation between rebound and friction is shown in Table 3, where increasing amounts of styrene,

TABLE 3

REBOUND, INTERNAL FRICTION, AND DYNAMIC MODULUS
(Tread stocks at 100° C)

Butadiene/Styrene	Dynamic modulus (G)	Friction (η)	Rebound (%)
100/0	26.5	7.8	62
85/15	21.1	7.9	72
72/25	17.4	7.7	47
60/40	14.1	7.9	42

for ratios 85/15, 75/25, 60/40, in the GR-S polymer result in a large decrease in rebound in tread stocks at 100° C, but cause no appreciable change in the friction. At 40° C, the friction increases with increasing styrene content, in agreement with the decreasing rebound.

A comparison of various hysteresis indices obtained by free vibration, forced vibration, and rebound methods is given in Table 4. The free vibration apparatus used was similar to that of Mooney and Gerke[37], except that moulded cylindrical samples were employed, and the torsion pendulum was pivoted on a needle point to allow measurements with no tension in the samples. While

TABLE 4

VALUES OF $p\eta$ FOR FORCED VIBRATION, FREE VIBRATION, AND REBOUND

| | Tests at 50° C | | | | | Tests at 100° C | | | | |
| | $G \times 10^6$ | | Values of $p\eta \times 10^6$ | | | $G \times 10^6$ | | Values of $p\eta \times 10^6$ | | |
Stocks	Forced vibra-tion	Free vibra-tion	Forced vibra-tion	Free vibra-tion	Rebound	Forced vibra-tion	Free vibra-tion	Forced vibra-tion	Free vibra-tion	Rebound
Hevea gum	3.0	3.8	0.20	2.08	0.565	3.1	4.7	0.13	2.52	0.415
Tread	19.5	28.4	3.81	24.2	6.9	16.1	19.0	1.00	9.40	5.4
GR-S gum	4.6	4.4	0.76	2.58	1.9	3.9	6.0	0.43	3.77	1.28
Tread	41.2	27.0	6.55	21.8	28.0	18.3	18.8	3.20	12.9	13.1

NOTE: Forced vibrator tests at 60 cycles per second.
Free vibration tests—torsion pendulum; frequency range—0.02 to 0.07 cycles per second.
Ball rebound tests: $p\eta = \dfrac{3G}{\pi} \ln \dfrac{100}{R}$: Forced vibration values of G used in calculation.

poor agreement was found for absolute values of $p\eta$ obtained by the various methods, the relative values for different stocks do not vary greatly. Undoubtedly the use of a more precise free vibration method would give better agreement in the absolute values of $p\eta$.

TYPICAL RESULTS OF HYSTERESIS MEASUREMENTS ON GR-S TYPE POLYMERS

The effects of varying the butadiene/styrene ratio are quite definite. It is observed in Figures 24 and 25 that increasing the styrene content of the polymer increases the friction. However the differences in η tend to diminish at high
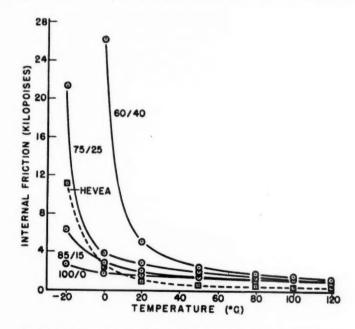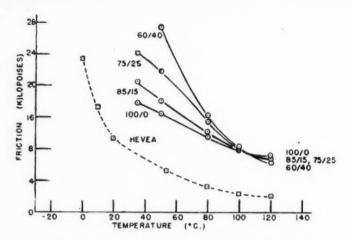
FIG. 24.—Butadiene-styrene ratio comparison; internal friction *vs.* temperature; gum stocks (Firestone resonance vibrator).

temperatures; whereas, as shown for tread stocks in Figure 27, the spread in dynamic modulus increases. This behavior is in accord with current theories of the structure of high polymers, increased branching (with decreased styrene) resulting in lower internal friction and a higher modulus. The increase in the

Fig. 25.—Butadiene-styrene ratio comparison; internal friction vs. temperature; tread stocks (Firestone resonance vibrator).

temperature coefficients with increased styrene is, perhaps, not quite so easily explained. The same tendency is shown in Table 5, where the dynamic properties for three states of conversion of GR-S in gum stocks are given.

The dependence of dynamic properties on the state of cure of a typical GR-S tread compound is shown in Figure 28. Formulas of the compounds used in the Firestone tests are given in Table 6.
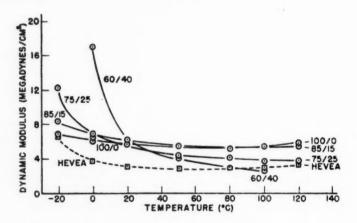
Fig. 26.—Butadiene-styrene ratio comparison; dynamic modulus vs. temperature; gum stocks (Firestone resonance vibrator).

TABLE 5

EFFECTS OF HYDROCARBON CONVERSION
GR-S in gum stocks
Tests at 60 cycles per second

Conversion (%)	Dynamic modulus (megadynes per sq. cm.)		Internal friction (kilopoises)		Rebound (%)	
	20° C	80° C	20° C	80° C	20° C	80° C
56	5.2	2.8	3.1	1.9	54	50
80	6.0	4.3	2.8	1.5	57	67
90	5.7	4.6	2.0	1.4	65.5	74
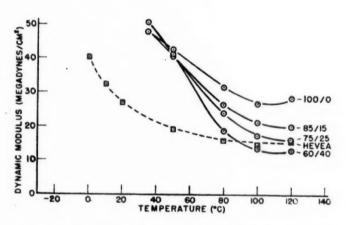
FIG. 27.—Butadiene-styrene ratio comparison; dynamic modulus vs. temperature; tread stocks (Firestone resonance vibrator).
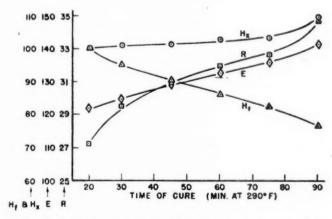
FIG. 28.—Effect of cure on dynamic properties; tread stock at room temperature (Goodyear forced vibrator).

TABLE 6

COMPOUND FORMULAS

(These apply to Firestone tests only)

	Hevea			GR-S	
	Gum	Tread		Gum	Tread
Rubber	100	100		100	100
Sulfur	3.0	3.0		2.0	2.0
Zinc oxide	3.0	3.0		5.0	5.0
Stearic acid	0.5	3.5		0.5	3.0
Captax	1.0	1.0		1.5	1.5
AgeRite Powder	1.0	1.0			
Pine tar		3.0			
Bardol					5.0
Channel black		50.0			50.0
Cure (min. at 270° F)	75	75		100	125

SUGGESTIONS ON METHODS OF EVALUATION OF EXPERIMENTAL POLYMERS

The foregoing analysis yields the following suggestions on hysteresis evaluation of experimental polymers.

1. Disregard results of static hysteresis loop measurements.

2. Question of all impact resilience values where modulus or hardness varies appreciably.

3. Avoid the use of free vibration measurements.

4. Make measurements at both room and elevated temperatures.

5. Make comparisons at the same frequency if possible (20 cycles per second, or higher).

6. Employ either constant amplitude or constant force indices, as demanded by the service application.

7. Internal friction or temperature rise under constant amplitude conditions appears to be the most reliable indices of the hysteresis defect, from a fundamental viewpoint.

8. It is desirable to make hysteresis measurements on both a gum stock and a tread stock of each polymer.

To recapitulate, the importance of laboratory hysteresis tests for synthetic rubber is twofold. In the first place, if properly carried out and interpreted, such tests enable a prediction of heat generation and relative service temperatures in various applications. In the second place, the tests furnish, in a general way, a criterion of the rubberlike quality of the polymer, its ability to deform and recover under the action of rapidly applied forces. The various deteriorating chemical reactions which comprise the aging of rubber all have positive temperature coefficients. When operating conditions are severe enough to cause appreciable temperature rise due to hysteresis, it seems obvious that the service life is adversely affected by the higher temperatures, not only because of accelerated aging, but also because of reduced hot tear and tensile values.

It seems well to consider briefly the desired characteristics of a dynamic test (or, in fact, any test) balanced against what we can expect actually to obtain. The natural question is often asked:

"What is the true index of dynamic quality in a polymer?"

It should be emphasized that there is not and never will be a unique answer to this question. The polymerization chemist and compounder must recognize

this fundamental fact if they ever expect to achieve an unambiguous concept of dynamic quality and clarify the objects of new polymer development. The reasons for this rather complicated state of affairs are readily evident. In the first place there are several dynamic properties, and these properties are not simply dependent. It is not possible to choose any one of these properties (resilience, internal friction, hysteresis at constant force, dynamic modulus, etc.) as the quality index. Various rubber products operate under widely different conditions of strain, rate of strain, stress, rate of stress, and temperature. Furthermore different conditions are not too clearly defined at the present time. It is evident, therefore, that there are as many quality indices as there are sets of product service conditions. Thus, instead of struggling to develop a universal ideal polymer, several polymers (appropriately compounded) should be developed along the lines suggested for their respective intended applications.

Acceptance of these facts should preclude toying with arbitrarily devised composite indices. The temptation, however, to combine several important physical properties into a "universal quality index" is strong, and a word of warning may not be out of place. Such a composite index can never have more than limited empirical success for the same reasons that no simple dynamic property can ever be expected to serve as a guide for polymer development or compounding for more than one set of service conditions.

ACKNOWLEDGMENT

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A SIMPLE COLD TEST FOR
VULCANIZED POLYMERS *

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The freeze resistance of vulcanized polymers has been evaluated for the past two years at this laboratory by a method which involves measurements of primary creep at successively lower temperatures. This method has been found to be particularly useful when it is desired to know, within 5° or 10° F, the temperature at which the polymer ceases to function as a rubberlike material. In a laboratory of this kind, where considerable work is done in evaluating new polymer types and where the polymerization variables studied often are of such a nature as to produce relatively large changes in the freeze resistance of the vulcanized polymer, a tolerance of 5° to 10° F has been found to be a workable value. The test is simple and can be carried out with the Shore A durometer or the A.S.T.M. hardness tester, one or both of which are generally available in a rubber laboratory. Its simplicity notwithstanding, the test is reasonably objective.

Both the durometer and the A.S.T.M. tester are handled in the conventional manner, and readings are taken five and 30 seconds, respectively, after the pressure plate or presser foot contacts the specimen. The degree of creep is recorded as the difference in hardness points between these two readings.

It is a matter of experience that, for most polymers, the amount of creep or flow exhibited at successively lower temperatures increases gradually, reaches a maximum, and then begins to decrease at a relatively high rate. The temperature at which this rapid drop-off occurs is considered significant because at this point the polymer begins to lose, at an accelerated rate, the fluidity which it had at higher temperatures and is being transformed into a hard, nonrubberlike material.

DETAILS OF TEST METHOD

In running the Shore hardness decadence tests, this laboratory uses a cabinet of the mechanical convection type cooled with solid carbon dioxide. The specimens, which measure two by $1\frac{1}{4}$ by $\frac{9}{16}$ inches, are mounted on a circular stage which can be revolved from the outside by means of a gear system. The durometer, kept inside the cabinet during the tests, is attached to a steel shaft which extends through the top of the box and is free to move vertically. The rod is weighted at the top to provide the proper pressure on the durometer. Readings are taken through a window mounted in the front wall. The interior of the box is illustrated in Figure 1. The cabinet need not be so elaborate as this to obtain satisfactory results. This apparatus was designed for convenience and speed in handling a large number of samples. Although the durometer may be hand-actuated, experience with this instrument indicates that gravity-actuation is considerably more desirable. The samples should be at

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least ½-inch thick and the lateral dimensions large enough to permit eighteen to twenty-four readings at different points on the surface.

The A.S.T.M. tester is used in conjunction with a sample conditioning bath of methanol. Solid carbon dioxide is used as the cooling agent. A slight modification was made in the instrument for the purposes of this test; the presser foot and indentor shaft were extended to a length of about eight inches to permit tests to be run under the methanol while the body of the tester is supported above the liquid on the edge of the tank. The modified instrument
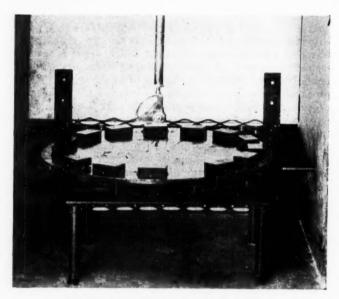
Fig. 1.—Cold test apparatus using Shore durometer.

is shown in Figure 2. The tank (not shown) is made of galvanized sheet iron, insulated with rock wool, and is contained in a wooden frame. The presser foot and indentor point extend into the methanol to a distance of about two inches. This is sufficient to maintain the indentor point and that portion of the presser foot which contacts the sample at the proper temperature.

TEST RESULTS

Figure 3 presents graphically a set of Shore durometer creep data for four polymers: (1) a tripolymer of butadiene, styrene, and acrylonitrile; (2) a tripolymer of butadiene, styrene, and methacrylonitrile; (3) a copolymer of butadiene and acrylonitrile, and (4) a copolymer of butadiene and methacrylonitrile. The corresponding monomer ratios are given. Each polymer was compounded with 50 parts of EPC black. It has been the practice to select as the "freeze point" the first point on the rapidly falling portion of the curve. Two independent observers may choose, from the same set of data, freeze points which differ by 5° F and, in some instances, 10° F. More often they choose the same point. The freeze points selected from the four curves illustrated are indicated by arrows on the figure.

Fig. 2.—Modified A.S.T.M. hardness tester.
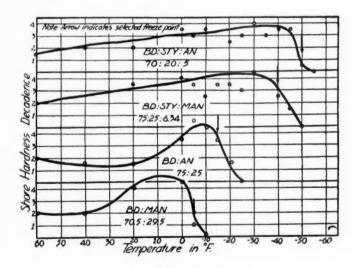
Fig. 3.—Shore durometer creep data.

Table 1 gives typical Shore and A.S.T.M. creep values for GR-I, GR-S, and natural rubber, each compounded with 50 parts of EPC black. The freeze points can often be determined without constructing the curve, as was done in this case.

TABLE 1

CREEP VALUES

Temp. (° F)	Shore durometer				A.S.T.M. tester		
	GR-I	GR-S	Natural rubber		GR-I	GR-S	Natural rubber
60	2.5	2.5	2		8	5	4.0
40	2	3.5	1.5		7.2	3.7	4.4
20	3.5	3	2		8.2	4.8	4.0
0	5	4	1.5		7.8	5.2	3.4
−5	5.5	4.5	2.5		9.8	3.5	3.9
−10	7	3.5	1.5		8	4.5	3.4
−15	6.5	2.5	2		9.2	4.5	3.5
−20	7.5	4	3		8.2	4.3	3.2
−25	7	4	3		9.2	4.2	4.8
−30	8	3	2.5		9.7	4.0	4.0
−35	6	3	3.5		6.6	3.9	4.5
−40	5	3	4		6.5	3.8	4.9
−45	4	3	3.5		5.4	3.5	3.8
−50	4	1.5	3.5		4.1	2.5	3.5
−55	3	0.5	3.5		3.1	1.8	3.7
−60	1	0	2		2.7	0.5	3.9
−65	0.5		1		1.5	0	3.9
−70	0		0.5		1		0.3
−75			0		0.4		0.4
Freeze point (° F)	−35	−50	−60		−35	−50	−70

MOULDING ANISOTROPY*

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It has long been an accepted fact that the properties of vulcanized rubber articles are not uniform in all directions. Vulcanized rubber is, in general, an anisotropic material, and the results obtained from tests vary, to a greater or less extent, with the direction in which the strain is applied or the measurements are made. In much experimental work elaborate precautions have been followed whereby replicate samples have been taken in the same directions from the rubber material.

The cause of anisotropy has always, as far as the authors are aware, been attributed to the methods of processing or shaping the raw stock. This is the view taken by the authors of one of the most recent publications[1]. As calendering is an operation that produces an extreme distortion of the raw stock, such processing effects are considerable, and the resulting anisotropy has been known for many years as calender grain, or in appropriate cases, as extruder grain.

It has been evident, however, for some years that the theory that the method of preparation of the raw stock is the sole or even the major cause of anisotropy is not adequate to explain certain phenomena. Some products exhibit pronounced anisotropy, although their method of preparation does not involve much distortion of the raw stock, and in other cases, such variation in properties as does exist does not give any correlation with the direction of processing.

Consideration of cases such as these have led to the conclusion that the movement of the stock during moulding is an important factor in the problem, and one that, as far as can be seen from the literature, has been hitherto neglected.

THE TEAR–DOWN ADHESION TEST

Solid Tires.—Ever since solid tires have been made, it has been customary to assess the adhesion of the tread to the base by measuring the force required to tear away a strip of rubber around the tire. It soon appeared that the pull required depends on the direction in which the test is applied, and that the highest and lowest bond tear strengths occur in opposite directions at any particular point on the circumference.

Another marked feature in the majority of cases is the abrupt transition from a high to a low tearing force that occurs when the strip is being torn steadily in one direction. Of special interest, however, is that at one of these transitions from, say, high to low tear, a tear made in the reverse direction shows a similar transition from high to low at the same place. In other words, a high tear in one direction is associated with a low tear in the reverse direction and *vice versa*, and changes in the character of tear are abrupt and at the same place, whatever the direction of tear. Generally two such transitions occur around the circumference of a tire, but there may be more.

This tearing is a tearing of the rubber, not a bond failure. It shows one other important characteristic. The low strength or easy tears occur close to, but not actually at the junction of the tread with the base, a thin film of rubber being left. The hard tears, however, are always associated with a tendency of the tear to turn upwards into the body of the rubber. In short, easy tears run down to the base, whereas hard tears run away from the base.

These observations, which are still true today with direct bonded tires, obviously suggest some kind of anisotropy in the rubber which decides the direction of tear. In the early days of tires built from calendered sheet, this was attributed to calender grain. When extruded treads became the rule, the concept of extruder grain was introduced to continue this interpretation.

When tires directly bonded to the metal by the brass plate process became general, an interlayer or "tie-gum" of a compound specially suited to bonding was often used between the steel base and the tread. This gave an opportunity for the calender grain theory to be tested, and experimental tires were made up in which the base layers were made from sections of calendered sheet, with the grain going in all directions. In these tires the directional effect of hard and easy tears was as definite as ever, but the runs of hard or easy tearing were quite unaffected by the boundary of the different sections, and the transition points bore no relation to the calender grain of the base stock. This experiment proved conclusively that, in these circumstances at any rate, the directional effect is not due to calender grain.

This directional effect is shown equally well on flat plates, such as are used for bonding experiments. A typical example is shown in Figure 1, where the loads are indicated at various points during the process of tearing strips in opposite directions along the whole length of a test-plate. The difference in appearance between the hard and easy tears should be noted. These conditions apply strictly only when the bond is sound and tearing occurs in the rubber.

Data from another test-slab are given in Figure 2.

This latter diagram illustrates the suddenness of the transition, and the considerable difference in load between the hard and easy tears.

Examination of large numbers of such plates led to the interesting observation that the easy tear, in the great majority of cases, was towards the edge of the plate (see Figures 1 and 2). An analysis of some tests is given below.

TABLE 1

ORIENTATION OF EASY TEARING DIRECTION IN TEST-PLATE

	No. of cases
Easy tear towards edge of plate	140
Indefinite (variation less than 5 lbs.)	75
Easy tear away from edge of plate	9

The number of cases in which the easy tear is towards the edge is by far the greatest. In the opposite cases, the difference in load was barely larger than the experimental error. It can, therefore, be asserted that when any difference between directions exists, the easiest tear is towards the edge of the plate. This, and the fact that a change in tear occurs in a large proportion of the plates, together with a definite orientation of tear, effectually dispose of any chance of the effect being due to calender grain. The only hypothesis that seems adequate to explain these results is that the *directional effect is due to the outward flow of rubber during moulding*. More careful examination of solid tires then showed that the easy tearing directions were toward the part
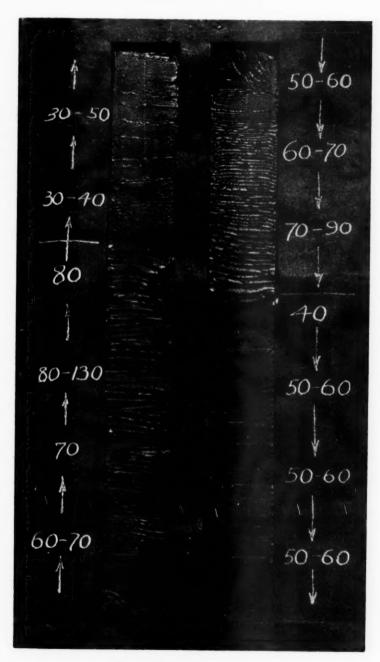
Fig. 1.—Typical tear-down test-plate.
(Arrows indicate direction of tear, numbers give force in lbs. to cause tear-down.)

of the tire which had the heaviest spew, in other words, were associated with a probable general drift of material round the tire during moulding.

Directional Effects in Transfer Mouldings.—It has been suggested that injection or transfer moulding would give more uniform products, as the method of filling such moulds would effectually destroy calender grain in the raw stock, and that movement of material in the mould would be more or less random and have no preferred direction.
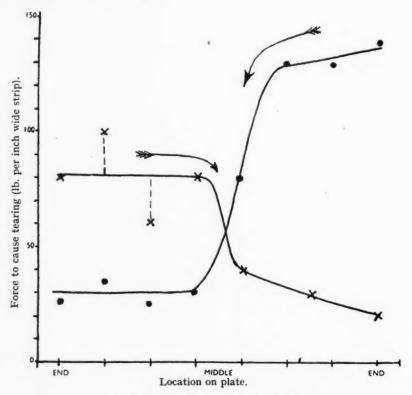
FIG. 2.—Force to cause tear-down on test-plate.
(Arrows show direction in which the tear was made.)

Actual experiment, however, shows that the second assumption is incorrect. A series of experiments on the flow of material in transfer moulds, made by using raw blanks built with layers of different colored rubbers, showed that after the mould was filled, a general movement of the material occurred in directions which were quite definite and repeatable for any particular mould. The experiments established that rubber during moulding behaved like any other fluid, and moved from regions of high pressure to those of low pressure. The result is that if any area of low pressure existed in the cavity of a transfer mould, the rubber as a whole would drift around to this point. Such areas of low pressure were found to be made by quite trivial causes, such as a partly choked injection hole or, most commonly, by a leak caused by accidental damage to the edge of the cavity.

An example of such a leak at D and the resulting flow is shown in Figure 3, and it is interesting to note in passing how the material flows and eddies round obstructions, as in photographs of air or water flow.
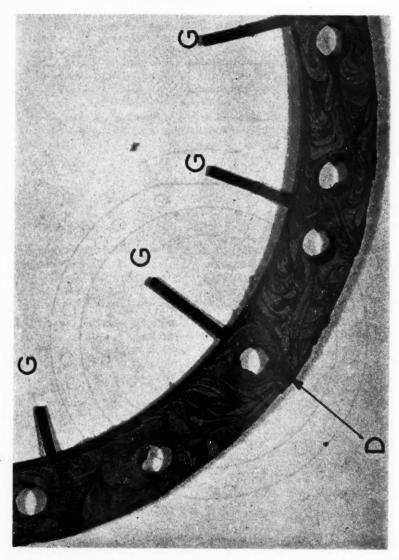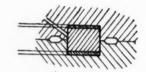
FIG. 3.—Flow resulting from leak at spew line due to mould damage at D.   (G are injection inlets.)

For the subject of this paper, however, these mouldings were more important, as the existence of such movement during moulding gave an opportunity of testing the hypothesis formed on the basis of solid tires and flat plates.   An injection moulding was therefore made in an appropriate compound, and the

rubber carefully torn from the metal in two opposed directions.   The results
agreed perfectly with the previous evidence, the transitions occurring at the
change of flow as indicated by the colored mouldings.   This is illustrated in
Figure 4.   In this diagram of a ring mounting, the rubber flow is shown by the
external arrows, and the direction of easy tear by the inner ones, the transition

Radial Cross-Section of Ring in Mould
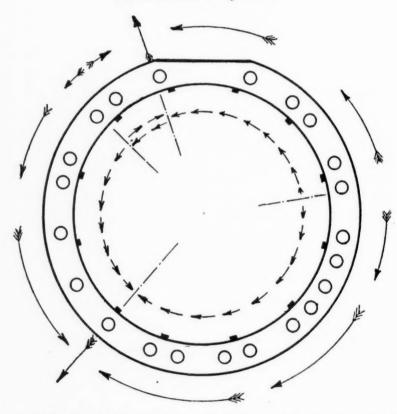
Fig. 4.—Details of flow and directional tear in ring mounting.   (External arrows show rubber flow.
Radial arrows show leak points.   Internal arrows show direction of easy tear.)

points being marked by radial chain dotted lines.   The position of the injection
holes is indicated by square black dots.   It will be seen that the tearing is
completely controlled by the final flow of rubber in the mould.   As before, the
easy tears were characterized by a thinner film of rubber left on the base, as
well as a lower force.

This experiment finally proves the point that tearing is easy and moves towards the base when made in the direction of mould flow, and is difficult and moves up into the rubber when made in opposition to the mould flow.

The Magnitude of the Directional Effect.—The numerical difference between the hard and easy tears depends on the compound used. Some compounds show little effect; others, especially those used in solid tires, give considerable differences.

The following figures were obtained in a test on brass-plate bonding, described elsewhere[2]. A base compound was prepared, and from this eight derivatives were made by varying the accelerator, zinc oxide and sulfur, as shown in the table.

TABLE 2

EFFECT OF SULFUR AND ACCELERATOR ON DIRECTIONAL EFFECT (TEAR-DOWN TEST)
Base mixing: Rubber 100, Gas black 30, Stearic acid 3

	AC	ABC	C	AB	BC	A	B	(1)
Mercaptobenzothiazole	1	1	$\frac{1}{4}$	1	$\frac{1}{4}$	1	$\frac{1}{4}$	$\frac{1}{4}$
Sulfur	8	8	8	3	8	3	3	3
Zinc oxide	5	30	5	30	30	5	30	5
Average high figure (lbs.)	97	93	98	106	92	68	87	87
Average low figure (lbs.)	24	21	31	53	49	33	68	75
Directional effect (difference)	73	72	67	53	43	35	19	12

From this table it appears that an increase of vulcanizing ingredients increases the directional effect, and a statistical analysis confirms that the effects of sulfur and of accelerator are highly significant.

THE EFFECT OF MOULD FLOW ON SHRINKAGE

An interesting corollary to this work on tear-down was discovered by A. Crothers[3]. A number of discs had been made from a mould that was truly circular and uniform in depth. On examination, however, the discs were found to be uneven in thickness and slightly elliptical. A study of fourteen discs showed a close correlation between the edge thickness of the discs and the diametral contraction, the latter being greatest where the edge was thickest. A typical example is given in Figure 5, which shows the measurements on six diameters at equal angles on one of the discs.

The variation in thickness was found to be due to a bent mould lid, giving an uneven spew gap. As the flow of rubber would be greater where the gap was widest, these results were interpreted as showing that the contraction was greatest in the direction of maximum flow.

THE EXPERIMENTAL PRODUCTION OF MOULDING ANISOTROPY

Crothers' results[3] seemed to establish the existence of dimensional anisotropy due to the flow of rubber in a mould, and in view of the increasing importance attached to dimensional accuracy in many rubber articles, it was decided to make a mould in which the outward flow would be in a definite direction.

The mould is shown in Figure 6 and consists of a cavity $6\frac{1}{2}$ inches square, with most of one side cut away. When the plunger lid is driven home, the mould is just closed to give a sample $6\frac{1}{2}$ inches square by $\frac{1}{16}$ inch thick, but until the mould is entirely closed, the rubber is able to flow freely through the open side.
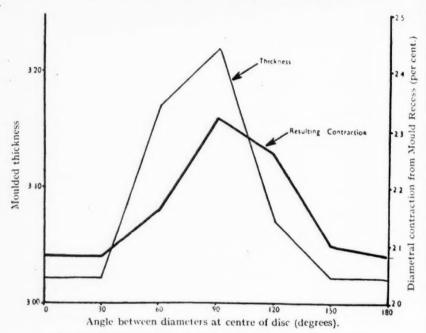
Fig. 5.—Typical measurements of moulded disc, showing correlation between moulded thickness and diametral contraction.
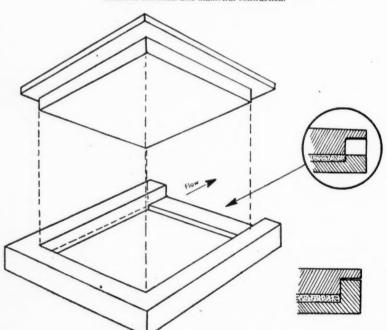
Fig. 6.—Mould to produce flow during vulcanization.

EXPERIMENT I.—Two compounds were used: (1) natural rubber, 100; zinc oxide, 25; lamp black, 55; sulfur, 3; mercaptobenzothiazole, 0.6; tetramethylthiuram disulfide, 0.2; and (2) GR-S, 100; black, 49: mercaptobenzothiazole, 1.75; diphenylguanidine, 0.2; sulfur, 2; softeners, etc., 6. Both had a nominal hardness of about 60° Shore. The stocks were prepared in the form of calendered sheet about $\frac{1}{16}$ inch thick. Eight mouldings were made of each compound, with 1, 2, 3 and 4 thicknesses of material, cut to fit the mould. In each compound, one set of four was arranged with the direction of calendering in the direction of mould flow; another set with the calender grain across the mould flow.

The samples were moulded for 25 minutes at a steam pressure of 60 lbs. per sq. in. in a daylight press having a 9-inch ram, giving about 100,000 lbs. total pressure.

Shrinkage.—Four fine lines were scribed on the lower face of the mould, near the edge, so as to enclose a square of 6-inch side. The distances between the intersections of these lines were measured, and from these the percentage shrinkages were calculated. The positions and directions of the measurements are shown in Figure 7.
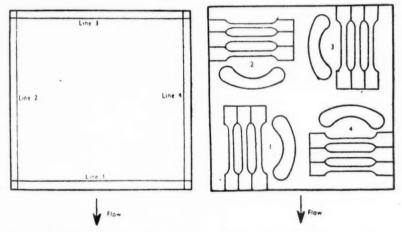
FIG. 7.—Location of measurements made on slabs.

FIG. 8.—Samples for tensile strength and tear from slab (see Figure 7).

The table shown on top of page 872 gives the measured shrinkages on all sixteen samples.

On statistical analysis of the results for the natural-rubber compound, it is found that the variation of shrinkage between lines and the effect of the number of plies are both highly significant. In the GR-S compound, only the line variation is significant though this is highly so. In neither case is there any significant effect due to calender grain.

It is seen from the figures that the shrinkage varies consistently with the position in the mould. Without exception, in every slab, dimension 3 gives the lowest shrinkage and dimension 4 the highest. Position 3 (see Figures 7) is the farthest from the opening in the mould and is, therefore, presumably the position of least rubber movement.

The difference between 4 and the next highest, 2, is small, but consistent. It is difficult to account for this, as 2 and 4 are at the sides of the mould, but

TABLE 3
SHRINKAGE OF MOULDED SLABS
(As percentage shrinkage of the measured lines)

No. of plies	Line	Calender grain with flow				Calender grain across flow				Average
		1	2	3	4	1	2	3	4	
Natural Rubber Compound										
Across flow	1	1.70	1.65	1.70	1.85	1.75	1.50	1.75	1.95	1.72
	3	1.40	1.60	1.55	1.75	1.75	1.40	1.60	1.60	1.59
With flow	2	1.95	1.60	1.65	1.80	1.85	1.70	1.65	2.0	1.78
	4	2.05	1.65	1.70	1.85	2.00	1.80	1.80	2.05	1.86
GR-S Compound										
Across flow	1	1.85	1.85	1.90	1.85	1.75	1.75	1.80	1.90	1.82
	3	1.50	1.50	1.50	1.50	1.40	1.50	1.35	1.45	1.44
With flow	2	2.05	2.15	2.20	1.90	1.85	1.85	1.95	1.85	1.95
	4	2.10	2.15	2.20	1.95	2.15	2.15	2.25	2.15	2.15

it may be connected with some cross-flow, due to unevenness in the mould. In the natural rubber samples, side 4 was the thickest part, followed by 3, 1 and 2, in order. In GR-S too, side 4 was thicker than 2. If the spew gap were wider on side 4, the flow would tend to be greater that side, which might have a bearing on the results.

The shrinkages of dimensions parallel to the flow (2 and 4) are higher than those across the flow. This agrees with Crothers' results. The effect of calender grain, on the other hand, is negligible.

The amount of material put in the mould, and hence the amount flowing out, does not have any systematic effect on the shrinkage, although there are significant differences between the mouldings in the natural rubber mouldings. These differences are interesting in view of later work.

The Effect on Tear.—After the slabs had been measured, crescent tear test pieces and tensile samples were punched out as in Figure 8.

The GR-S compound did not show significant variation in tear, but the values for the natural rubber compound are of interest in the present discussion.

TABLE 4
TEAR TESTS ON MOULDED SLABS
Crescent tear (kg. per mm.)

No. of plies	Position	Calender grain with flow				Calender grain across flow				Average
		1	2	3	4	1	2	3	4	
Natural Rubber Compound										
Tear across	1	4.78	3.97	4.10	3.14	3.60	4.00	3.04	2.86	3.69
flow	3	3.17	3.14	3.50	3.33	3.14	3.94	2.91	2.82	3.25
Tear with flow	2	5.40	(5.84)	6.06	5.03	(5.72)	6.80	6.70	6.90	(6.06)
	4	6.68	4.60	5.04	6.45	4.60	5.35	4.97	5.67	5.42
Average		5.07	(4.39)	4.67	4.48	(4.26)	5.23	4.41	4.56	(4.60)

Note to Table 4.—The values in brackets were inserted in tables by the missing plot technique[4].

Table 4 shows that positions 1 and 3 give considerably lower results than 2 and 4. Test-piece 3 is, in all but one case, the lowest of each set. These results are statistically significant and in this respect the results are similar to those for shrinkage.

In the crescent-tear test, the tear is roughly at right angles to the direction of pull, so the tears of 1 and 3 are across the flow due to moulding, whereas 2 and 4 are parallel to the mould flow.

The effect of flow and calender grain can be compared.

TABLE 5

COMPARISON OF CALENDER GRAIN AND MOULD FLOW

Calender grain	With flow	Across flow
Tear across flow	3.64	3.29
Tear with flow	5.64	5.84

From Table 5 it appears that tear strength is greater across the calender grain than with it, but that the effect, as with shrinkage, is much less than that due to mould flow.

In this experiment, therefore, a compound has shown 70 per cent greater tear strength in a direction parallel to the mould flow than across the flow. It follows, therefore, that it is of little use arguing about 10 per cent or 20 per cent variation of tear strength between compounds, unless the directional effect is considered.

Again, neither compound shows any definite change of tear with the amount of rubber in the mould, but there is a suggestion of differences between mouldings due to an unknown cause.
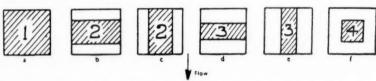
FIG. 9.—Diagram showing shapes of rubber used in mouldings referred to in Table 6.
(*Note.*—The numbers refer to relative thicknesses of stock before moulding.)

The Effect on Tensile Properties.—From tests on the same slabs, the effects of mould flow and of calender grain on tensile strength and modulus with these two compounds were found to be negligible. In view of the magnitude of the effects on shrinkage and tear that have been shown, the possibility that marked moulding anisotropy of these properties may be caused in suitable compounds must still be given serious consideration.

EXPERIMENT II.—To find whether the distance the rubber moved during pressing-up had any influence on the anisotropy, a series of mouldings of the natural rubber compound were made with the same weight of raw stock cut into various shapes as in Figure 9.

TABLE 6

EFFECT OF SHAPE OF RUBBER ON CONTRACTION OF RESULTING SLAB
(See also Figure 9)

	Line	Fig. 9a	9b	9c	9d	9e	9f
Across flow	1	1.48	1.51	1.51	1.51	1.54	1.44
	3	1.35	1.31	1.34	1.38	1.48	1.31
With flow	2	1.68	1.58	1.71	1.68	1.64	1.71
	4	1.77	1.71	1.90	1.74	1.68	1.71

The table shows that the shape of the blank has no effect on the shrinkage,

so that with this compound, at least, wide variations in the method of loading the mould do not affect the final result.

EXPERIMENT III.—Experiment I showed that the amount of rubber flowing from the mould had only a minor effect, and Experiment II showed that the movement of rubber to fill a mould did not alter the anisotropy. It seems, therefore, that *anisotropy must develop at a later stage, after the mould is filled,* and since anisotropy is definitely associated with direction of flow from the mould, the implication is that it must be connected with flow during the curing stage.

The next experiment was, therefore, designed to find at what stage of cure the anisotropy was produced.

The flow mould was held open by $\frac{1}{16}$-inch steel strips between the bearing surfaces, which had the effect of increasing the cavity depth to $\frac{1}{8}$ inch. A series of slabs was moulded, with the packing taken out at different intervals after the start of curing, which was then continued for a total time of 20 minutes at 307° F.

TABLE 7

EFFECT OF MOULDING PROCESS ON SHRINKAGE

	With flow	Across flow	Average	Condition of cured slab
(1) Normal moulding	1.7	1.8	1.75	Smooth
(2) Final closing 1 min. after	3.1	1.4	2.2	Distorted, uneven
(3) Final closing 2.5 min. after	4.1	0.7	2.4	Very distorted
(4) Final closing 5 min. after	3.2	2.0	2.6	Flat and thick

The uneven shrinkage of sample 3 was so pronounced that the sheet contracted violently immediately the mould was opened, tearing away from the spew and giving a twisted and wrinkled sheet.

These results indicate the cause, not only of uneven shrinkage but of the whole phenomena of moulding anisotropy. Uneven shrinkage is caused by a movement of rubber which has already begun to develop a cured structure. It is not unreasonable to assume that the directional straining of a partially developed structure is the cause of anisotropic effects produced during the moulding process. Furthermore the results show that a small amount of cure is sufficient to produce a structure which leads to anisotropy when subsequent flow takes place, even exposure of one minute to a temperature of 307° F giving a 2 to 1 difference in shrinkage, whereas with 2.5 minutes of the ratio is 6 to 1. After 5 minutes of cure, the rubber has become too stiff to move under the applied pressure, so that the conditions for uneven shrinkage are not present.

The normal moulding in this experiment shows no differential shrinkage, in contrast to the earlier results in this paper. This is probably due to more care being taken to avoid delay in closing the press, a view which is confirmed by the difference between mouldings in the earlier work which was commented on after Table 6.

THE EFFECT OF FLOW ON SWELLING

It has been observed by Scott[5] that the swelling of certain compounds in oil is greatest perpendicular to the plane of the rubber. This he attributes to calender grain.

An examination of this point was made by immersing 5-cm. squares cut from the test sheets of Experiment III in DTD.44D oil at 70° C overnight, and measuring the increase in length and thickness.

TABLE 8
Effect of Mould Flow on Swelling

Sample	With flow	Percentage swelling across flow	Thickness
1	28	30	28.5
2	23	29	36.5
3	27	30	36
4	27	29	34
Average 26.3		29.5	33.5

The results do not show a close correlation with those of Experiment III, but they do indicate that swelling is greater where flow is least, the difference between with- and across-flow being just significant ($P = 0.05$).

In another paper[6] Scott has made the interesting observation that some of his samples swollen in oil were anisotropic in tear, but in this case the tear was easiest in the direction parallel to the mould flow.

DISCUSSION

Anisotropy in rubber articles can be caused both in manufacture and in the laboratory by movement of the material during the moulding operation. This anisotropy often exceeds that due to processing, and it is exhibited in differential tear, differential shrinkage and uneven swelling in liquids. Although these limited experiments have not shown much effect on tensile properties, it is best to assume that, under appropriate circumstances, moulding would affect these also.

The evidence from production articles which show unintentional mould flow effects and evidence from laboratory tests on controlled flow are complementary, and the agreement between them confirms both the explanations put forward and the widespread importance of the effects.

The cause of anisotropy also seems to be clearly shown as movement of rubber that has already acquired some vulcanized structure. This vulcanized structure is strained by subsequent flow, and the completion of cure superimposes a further structure on the strained one. On removal from the mould, the article distorts until the initial and final structures are in equilibrium. It follows, therefore, that differential shrinkage is evidence of internal strain in the material, and this must be expected to modify the properties of the product.

As little as one minute at 307° F gives obvious anisotropy, and it is easy for sufficient structure to be formed early in the curing for the above mechanism to operate. Conversely, unless special precautions are taken, moulding anisotropy is difficult to avoid. The only way to reduce the effect is to arrange so that thermal and plastic equilibrium of the moulded stock is complete before any incipient vulcanization or scorching takes place. This also is a function of the curing properties of the compound, since differential tear decreases with decrease in sulfur and accelerator.

There seems to be no simple way of avoiding moulding anisotropy in many compounds, and it is important, particularly in experimental and research work, that the direction of flow should be known and the effects of flow allowed for in the tests. The fact that in one compound tear strengths may be 70 per cent greater along than across the flow makes the comparison of tear strengths between compounds much more difficult. In this respect the crescent-tear test is not satisfactory, since the direction of tear can only be

controlled to a limited degree. A test on the lines of that described by Cooper[7] would seem to offer possibilities of examining tear in specific directions, although the method of preparing the samples may introduce anisotropy.

The cause of the directional effect in the tear-down appears to be the deflection of the tear-up into the rubber or down to the base, for a preliminary mathematical analysis, considering the case of an elastic beam attached by an elastic layer to a rigid foundation, suggests that, for a given tear strength, the load required to maintain the tear is less, the nearer the tear is to the foundation. The deflection of the tear up or down can be shown to be consistent with the produced anisotropy in the other experiments by the following considerations. First imagine a circle in the plane of the raw stock used in the laboratory-slab experiments. The flow during moulding distorts this to an ellipse (Figure 10a) and, as has been shown, tear strength is lowest across the flow, that is, along the minor axis of the ellipse. Turning now to the conditions near a surface, high shears are developed when a plastic flows over a surface, and this has a similar effect of distorting an initial circle into an inclined oval shaped figure (Figure 10b). If tear strength is always lowest along the minor axis of the hypothetical oval, the tear tends to be deflected along the axis, and this has the effect of deflecting the tear towards or away from the base, according to the initial direction (Figure 10c).

It has been shown in this paper that rubber movement in the early stages of cure produces anisotropy, which is orientated to the direction of movement. When a moulding is taken as a whole, the orientation is along the general direction of flow, but as the movement of any small element of the moulding is along a streamline, the anisotropy is, of necessity, orientated along the streamlines. This means that at corners or other parts where the streamlines are curved, the local properties may have a different direction from that of the mass of the material.
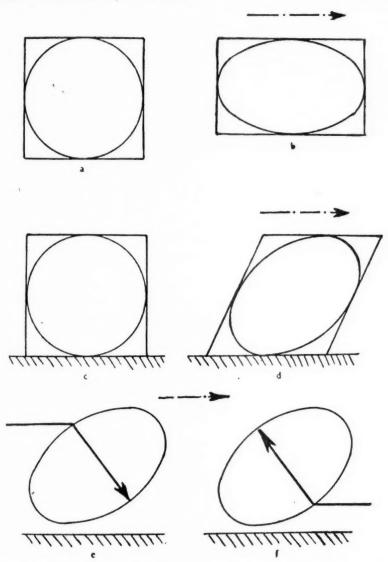
From this point of view shrinkage may be considered as the contraction of a streamline along its length. This has the important result that a high local contraction occurs where a number of streamlines leave the moulding. This explains the observed facts that mouldings tend to shrink most at the spew line and that a deep depression may be formed where there is high local flow due to damage of the mould edge or other cause. In the case of solid tires, the length of streamline may be half the circumference of the tire, and a small percentage contraction of a streamline may produce a hole of considerable magnitude. As an example, a differential shrinkage of 1 per cent on a streamline 50 inches long (say a 32-inch diameter tire) produces a depression approximately half an inch deep.

In connection with solid tires, it must be pointed out that the amount of spew is relatively small, and the general moulding anisotropy may be insufficient to obscure the calender or extruder grain, but the inevitably high shears close to the base always produce the directional tear effect.

In conclusion, it must be stated that the same mechanism serves to explain both moulding anisotropy and calender grain. The essential conditions would appear to be the existence of a strained structure in the raw material on which is superimposed a structure due to final vulcanization. Which of these two has the major effect depends on conditions. Calender grain, on this theory, may be expected to be high when a structure exists in the raw stock, either naturally, by set-up or by scorching, before processing; whereas mould flow effects are predominant in rapid curing stocks or cases in which thermal ex-

pansion is of importance. However, the resulting anisotropy can be expected to affect most of the properties of rubber, as subsequent tests involve the distortion of material already in a state of strain. With modern compounds and

Fig. 10.—Relationship between slab tests and tear-down tests. *a* Undistorted disc; *b* Distorted by flow; *c* Undistorted stock next to base; *d* Stock distorted by shear; *e* and *f* Deflection of tear due to easy tear being across the hypothetical oval.

techniques, such a condition is most difficult to avoid, and it is important that its existence and implications should be considered when tests are being designed.

ACKNOWLEDGMENT

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PROPER PRESERVATION AND STORAGE OF LATEX *

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During the war years, when the maintenance of a stockpile of natural rubber latex was of critical importance, great opportunities were offered to establish new and improved techniques for its preservation and storage.

Eight precautions are essential if latex is to be kept in good condition during long-term storage: (1) it should be kept free from bacteria; (2) it should have a sufficiently high pH level, which depends on the type of latex; (3) it should be maintained at uniform total solids; (4) its temperature should be uniform and properly regulated; (5) it should undergo minimum exposure to oxygen; (6) storage vessels should have smooth side walls and should be properly sterilized; (7) it should not be exposed to either indirect or direct light, and (8) it should have a low KOH number[1].

Every one of these items must be considered carefully if the latex is to be maintained at highest quality. Each one will be discussed separately.

DETAILS OF PRESERVATION PROCEDURES

When it arrives in this country, latex is generally free from bacteria, provided it originally was preserved properly. However, there are many opportunities for bacteria to enter latex; for example, in the ships or at the unloading stations. For this reason it is absolutely essential that there be no bacteria present. This means that latex which is to be stored for long periods of time should be tested for freedom from bacteria.

FREEDOM FROM BACTERIA

To test latex for bacteria special technique is required. The bacteria commonly found in ammonia-preserved latex have to be cultured in media on which they thrive. It is not within the province of this paper to give the definite technique necessary to do this. We would like to state, however, that either an aerobic or anaerobic culture can be made. Fairly accurate results from either method are obtained. The aerobic method requires about four days and the anaerobic method approximately three weeks.

It can be readily seen that if bacteria are present in latex to be stored, they soon multiply and cause great deterioration or damage to the latex.

If bacteria are found to be present, it is necessary to kill them. The proper way to destroy them depends entirely on conditions of storage as well as on the actual amount of infection. If the infection is not large and it is found that the pH level is low, owing to, say, insufficient ammonia, then in most cases only the addition of ammonia may be necessary.

If, however, the infection is great and the ammonia level seems correct, it is necessary to kill off the infection by more strenuous means. Some ma-

terials that can be used are sodium pentachlorophenol, trichloronitromethane, and other similar chemicals. These chemicals must be used in very small concentrations, especially the first one, as it is harmful to skin tissue. Chloropicrin is very effective in dilute concentrations, and since it breaks down after long standing, it is not harmful to the workers when processing the latex thus preserved.

SUFFICIENT AMMONIA TO PRESERVE pH LEVEL

Generally speaking, all commercial latices contain ammonia, at least in part, to preserve them. Some commercial latices have been treated before the addition of ammonia and for this reason do not require so much ammonia as those latices that have had no such treatment.

All latices for storage, whether concentrates or normal latex, should be maintained at a level above pH 10.2, preferably around 10.3. The concentration of ammonia to maintain such pH levels depends on the original preservation of the latex as well as on the condition of preservation at the time the level is readjusted. However, if the same degree of preservation is obtained in the samples examined, then the following amounts of ammonia are sufficient to maintain the pH level indicated.

Type of latex	Percentage ammonia
Normal latex preserved entirely with ammonia	1.2
Normal latex, 958 type[2]	1.0
Centrifuged latex preserved with ammonia	0.65
Centrifuged 957 type[2]	0.58
Creamed latex	0.65

It is necessary to examine latex in storage from time to time to see that these concentrations of ammonia or the proper pH levels are maintained. If examination is made and the latex was originally free from bacteria, there should be no worry from infection from outside sources.

MAINTENANCE OF UNIFORM TOTAL SOLIDS

The maintenance of uniform total solids is a very important precaution. Latex, whether it is concentrated or the normal variety, creams on standing; that is, the large globules and particles readily rise to the top. This action causes a concentrated layer of rubber or butter containing a low amount of serum in the upper part of the storage space. A considerable amount of creaming occurs in periods of one month, and worse conditions are encountered if the latex is not disturbed for longer times. As a matter of fact, normal latex can be creamed by standing two years in about as efficient a manner as it can be centrifuged in a few hours.

It can be seen that if this nonuniformity of solids is allowed, the actual concentration of the preservative varies from top to bottom, and the pH level drops in the thick butter layer at the top and proper preservation conditions are not obtained. To prevent this state of affairs, the latex should be agitated. One of the best ways to do this work is to agitate from the bottom, using a slow-speed chromium plated metal propeller turning at the rate of about 1,100 r.p.m. and agitating the latex for about 10 or 15 minutes. One propeller can properly agitate a 10,000-gallon storage space without difficulty. When the storage space reaches 20,000 or 30,000 gallons' capacity, it is advisable to use two such propellers, placed at opposite corners of the storage tank. Such a

procedure, if carried out every month or six weeks, should maintain the total solid distribution in pretty fair condition. It is easy to check the distribution of total solids by taking samples from the bottom, the middle portion, and the top of the storage tank and by examining what the differences are.

If metal propellers are not available, it is of considerable help to agitate the latex in the storage tank by means of compressed air. Introduce the compressed air at the bottom of the tank; if the tank is large, allow the air to blow through 10 to 15 minutes every four or five weeks. It must be understood that this method is vulnerable from the viewpoint of minimum exposure to oxygen. But it is better to maintain uniform solids and forego what difficulties may occur from the introduction of oxygen.

Other methods of maintaining proper total solids content can sometimes be applied where spacing conditions are available. This can be done by transferring the latex stored in one tank into another tank, using air pressure or vacuum, and reversing the procedure one or two times until thorough mixture is accomplished.

REGULATION OF TEMPERATURE

Latex should be stored at as cool a temperature as is possible, provided this is above the freezing point of water. These conditions are met best by having the storage tank located in the ground. This offers more or less constant temperature conditions, as the whole of the tank is subjected to approximately the same temperature. Where metal tanks, placed above the ground, are used, there are tendencies for the top of the tank to become warmer than the bottom of the tank or *vice versa*, and in such cases constant sweating occurs, which is undesirable. Metal tanks or any kind of tanks above the ground should always be protected from direct sun rays. If not, considerable coagulation and spoilage of latex directly on the metal wall will take place.

This point also applies in the transportation of latex. An insulated tank car is the best type of car in which to ship latex, either in hot or cold weather. Noninsulated metal cars are not suitable for storing latex any length of time.

MINIMUM EXPOSURE TO AIR OR OXYGEN

There is very little to say on this point. What is desired is to protect the latex from being oxidized. Anything that can be done to keep oxygen away is helpful. Low temperatures of storage also are helpful. The application of ammonia vents in storage tanks generally insures an ammonia gas layer above the latex and prevents continual seepage of fresh outside air. This arrangement can be made by putting an ammonia trap at one of the vents.

PROPER STORAGE VESSELS

Under the subject of regulation of temperature it was stated that the best place for storing latex is in the ground. It is our experience that the type of vessel best suited for storing latex is a concrete tank. This tank can be practically any size desired from 20,000 to 40,000 gallons. It must be so equipped with proper pumps that latex can be pumped in or out of the tank. The concrete must be of good variety, have a smooth surface and be properly coated.

The best method of coating concrete tanks is first to get the concrete dry. Sometimes it has been found necessary to put an electric oven into the tank and heat the tank until it is relatively dry. If this is done and if the concrete walls

are fairly smooth, the next step is to coat the walls with molten paraffin, which can be either sprayed or brushed on.   Both methods have been used successfully.   The coating should be put on as thin as possible; always be sure that the surface is completely coated.

Other combinations have been used; for example, mixtures of paraffin and asphalt, mixtures of paraffin and chlorinated rubber, and chlorinated rubber itself, but for concrete storage tanks which are in the ground and are not exposed to high temperature, molten parffin is about as good a coating as can be used.

Such a coating prevents the latex from adhering to the sides of the concrete tank.   It makes easy cleaning of the tank on removal of the latex, and the hot paraffin application on the side walls also goes a long way toward sterilizing the tank before the latex is introduced.

After the paraffin coating has set, and before any latex is introduced into the storage tank, the tank should be completely fumigated by means of formaldehyde.   This fumigation can be accomplished by burning a paraformaldehyde candle in the tank.   The customary dosage is 100 grams of paraformaldehyde per 10,000 gallons of space.   While burning the candle, allow the tank to be closed for 24 hours before use.

EXPOSURE TO LIGHT

Of course there is not much point to this precaution, since concrete and steel tanks are not exposed to light, but glass bottles, demijohns, and the like should be stored in darkness for the best results.

LOW KOH NUMBER

When latex deteriorates, acid is formed.   This can be detected by making a KOH number determination.   Here is another tool which can be used to find out whether latex is bad or is going bad.

HOW LONG CAN LATEX BE STORED?

The answer to this question depends a good bit on how the latex has been stored.   We have had latices that have remained in good shape after ten years of storage.   However, at the end of ten years there is some deterioration which involves mostly the nonrubber components, but in part the hydrocarbon itself.   It is our experience that, with proper storage conditions, latex can readily be maintained in good condition for three years and in very fair condition for five years, and that it is possible to maintain latex for ten years and still be able to use it.   We do not advise, however, this long period of storage unless absolutely necessary

The biggest difficulty with storing latex is the breakdown of the nonrubber components.   This causes formation of acidic substances in the latex.   Hence the KOH number rises over long periods of storage, independent of whether the conditions of preservation are correct or incorrect.   Of course the KOH number rises faster if the conditions of storage are incorrect; nevertheless, even when perfect conditions are met, the KOH number increases with time.   This rise is a minimum when the latex is stored at the lowest temperature or when there is a minimum amount of oxygen.

Sometimes the KOH number rises to such a point that it becomes difficult to handle and compound the latex.   This difficulty can readily be overcome by

proper purification of the latex itself.   One of the best ways is to recream the latex.   This is not too expensive, and it puts the latex in condition so it can be used as readily as new or recently tapped latex.

There may be conditions when the whole quantity of latex does not need to be recreamed, and then it is necessary only to recream part of the latex and mix the two parts together.   To one experienced in the art, it would be very simple to employ this recreaming process to advantage under almost any circumstances usually encountered.

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CONTROL OF pH OF NEOPRENE LATEX*

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One of the major contributions to the development of the use of rubber latex in manufacturing processes has been the introduction of methods for regulating the pH of the latex compounds[1]. On the basis of this knowledge the coagulating dip process, the use of heat-sensitive latex mixes, and the use of gelling agents have become standardized and accepted methods of manufacturing rubber goods.

Most of the techniques used in rubber latex manufacturing processes have been applied to the alkaline Neoprene latices, such as Types 571 and 60. However, in the case of the gelling agents the methods normally used to control coagulation of natural-rubber latex do not always apply to Neoprene latex. An investigation was made of the effect of pH reduction on the reaction between Neoprene latex and gelling agents, and also of methods for the control of this reaction.

The effectiveness of the gelling agents as coagulants arises from the delayed formation of hydrogen ions or multivalent metallic ions in the latex which these agents produce under certain specified conditions. A good example of this phenomenon is the reaction that takes place when sodium fluosilicate is added to either natural rubber or Neoprene latex. The sodium fluosilicate hydrolyzes in the latex forming sodium fluoride, hydrofluoric acid, and silicic acid. Twiss and Amphlett[2] state that the reaction probably proceeds according to the following equation:

$$Na_2SiF_6 + 4HOH \rightleftharpoons 2NaF + 4HF + Si(OH)_4$$

Coagulation of the latex is caused by the hydrofluoric acid.

Commercial Neoprene latices are stabilized with rosin soap and excess alkali. Much or all of this alkali must be neutralized by the hydrofluoric acid formed by hydrolysis of the sodium fluosilicate before gelation of the latex can take place. The higher the initial alkali content, the greater is the time interval between the beginning and the completion of gelation. If the interval is too great, gel deformation occurs. There is some variation in the alkali contents of different lots of Neoprene latex. This results from the evolution of small amounts of hydrogen chloride during aging. Older lots of latex have a somewhat lower pH and alkali content.

Latex must be brought to a standard alkali content before sodium fluosilicate is added, if consistent results are to be obtained in gelling processes. This can best be done by reducing the excess alkali content to a definite value by adding a controlled amount of an acidic substance. The common acids, however, are not suitable for bringing about a controlled reduction in pH. Concentrated solutions of strong acids cannot be added to natural-rubber latex

without causing coagulation or flocculation, unless the latex is especially stabilized. Highly alkaline Neoprene latices are even more sensitive than natural-rubber latex to acidic coagulants. The highest concentration at which strong acids can be added is approximately 1 per cent, whereas even ordinary weak acids cause local coagulation at 5 per cent concentration. If it is desired to reduce the pH of a strongly alkaline Neoprene latex, very dilute acid solutions have to be used, and they cause a marked reduction in the solids content of the latex. Furthermore, if the acidic substance is not added cautiously, severe flocculation occurs.

In many cases it is not desirable to attempt to control coagulation time by varying the proportion of sodium fluosilicate added. The character of the gel obtained varies widely, depending on the pH of the starting latex and the concentration of fluosilicate. Consistent results can be obtained, however, if the pH of the starting latex is brought to a constant value before the fluosilicate is added. This can be accomplished by neutralizing a portion of the excess alkalinity in the latex with some acidic substance.

ACIDIC SUBSTANCES ADDED TO NEOPRENE LATEX

It was found that acids with an ionization constant below 5×10^{-6} do not coagulate Neoprene latex Type 571 or other alkaline Neoprene latices (Table I).

TABLE I
CORRELATION BETWEEN IONIZATION CONSTANTS OF ACIDS AND THEIR EFFECTS ON NEOPRENE LATEX

Acid	Concentration of aqueous solution added (g. per 100 g. water)	Coagulation of Neoprene latex type 571	K_H at 25° C	Reference
Oxalic acid	5	+*	10^{-1}	10
Phosphoric acid	5	+	7×10^{-3}	7
Malonic acid	5	+	1.6×10^{-3}	6
Chloroacetic acid	2	+	1.5×10^{-3}	6
Bromoacetic acid	2	+	1.4×10^{-3}	6
Tartaric acid	5	+	9.6×10^{-4}	6
Mandelic acid	10	+	4.1×10^{-4}	6
Formic acid	2.5	+	2.1×10^{-4}	6
Glycolic acid	10	+	1.5×10^{-4}	6
Acetic acid	2	+	1.8×10^{-5}	6
Formamide	Undiluted	−†	3.4×10^{-6}	14
Resorcinol	50	−	6×10^{-7}	6
Pyrogallol	50	−	6×10^{-8}	1‡
Succinimide	40	−	6×10^{-8}	15‡
Boric acid	5	−	6×10^{-10}	8
Catechol	40	−	3.2×10^{-10}	6
Phenol	8	−	1.1×10^{-10}	6
n-Butane sulfonamide	100	−	10^{-10}	§

* "+" indicates the latex was coagulated locally.
† "−" indicates no coagulation occurred.
‡ K_H was calculated from data given in these references.
§ K_H was estimated from titration data.

These weak acids can be added to latex as concentrated aqueous solutions, and no coagulation occurs, even when solution and latex are mixed with a minimum of stirring. When stronger acids are added as dilute or moderately concentrated solutions, they coagulate locally around each drop added to the latex, even though the amount of acid is far less than would be required to coagulate

the entire latex. Therefore, in reporting what agents do not coagulate latex, it is necessary to specify the solution concentration but not the amount added, since coagulation, if it is to occur, will be noted on the first addition. Preliminary experiments were carried out with solutions in the concentration range of 2–10 grams per 100 grams of water. If no coagulation resulted, higher concentrations were used until saturation was approached.

Although the data of Table I indicate that acids with ionization constants over 5×10^{-6} could not be added to Neoprene latex, it was found that amphoteric compounds with larger acidic ionization constants do not coagulate latex if they have basic ionization constants comparable in strength to their acidic ionization constants. The amino acids are obvious examples of such amphoteric compounds.

All of the common amino acids with solubilities of 10 per cent or more were tested in Neoprene latex Type 571. None of them coagulated the latex at the concentrations indicated in Table II, even though they had acidic ionization constants of 10^{-2} to 10^{-5}.

<div align="center">

TABLE II

IONIZATION CONSTANTS OF AMINO ACIDS

</div>

Acid	Concentration of aqueous solution added* (g. per 100 g. water)	K_H†	K_{OH}†
Glycine	23	4.5×10^{-3}	4.0×10^{-5}
Sarcosine	40	5.4×10^{-3}	10^{-4}
α-Alanine	12.5	4.5×10^{-3}	4.9×10^{-5}
β-Alanine	10	2.5×10^{-4}	1.5×10^{-4}
α-Amino-n-butyric acid	15	2.8×10^{-3}	4.0×10^{-4}
α-Amino-isobutyric acid	10	4.4×10^{-3}	1.6×10^{-4}
ϵ-Aminocaproic acid	40	3.7×10^{-5}	5.6×10^{-4}
Proline	20	10^{-2}	4.0×10^{-4}
Taurine	9.5	3.2×10^{-2}	5.5×10^{-2}

* No coagulation of Neoprene latex Type 571 occurred.
† Values reported by Cohn and Edsall[13].

Picolinic acid (pyridine-2-carboxylic acid) was another compound of amphoteric character which could be added to Neoprene latex Type 571 (as a 10 per cent solution) without causing coagulation, although large amounts seemed to have some destabilizing effect. No reliable data are available for the acidic and basic ionization constants of picolinic acid.

AGENTS FOR REDUCING pH OF NEOPRENE LATEX

From these results it can be concluded that a satisfactory controlled reduction of the pH of Neoprene latex can be carried out using water-soluble amino acids, phenols, amides, or imides. Water-insoluble compounds are not suitable because they require a special dispersing operation and because they react slowly with the latex, giving delayed and unpredictable effects. The ideal agent for reducing pH should be readily soluble in water, colorless, odorless, available, nontoxic, completely compatible with Neoprene latex, and free from delayed action effects.

The amino acids best fulfill these requirements, and glycine, the simplest amino acid, is probably the compound most suitable for use as a pH reducer

for Neoprene latex.   The compounds listed as noncoagulating in Table I have
the following disadvantages: formamide and succinimide tend to reduce the
pH slowly after addition, phenolic compounds introduce toxicity and odor
problems, n-butane sulfonamide has a high molecular weight, which necessi-
tates the use of larger amounts than for simpler compounds, and boric acid is
too insoluble to be completely satisfactory.

In all processes where high-solids latex is needed, such as in gelling or dip-
ping, it is important that the pH be reduced with the least possible dilution of
the latex.   If the pH is to be reduced to a value as low as 9.7, boric acid dilutes
the latex more than any of the organic compounds because of its low solubility
(Figure 1).

Concentrated resorcinol solutions give the least dilution (Figure 1), but
resorcinol is undesirable because of its phenolic odor, colored oxidation products,
and toxicity[10].   Catechol has the same disadvantages and, in addition, is less
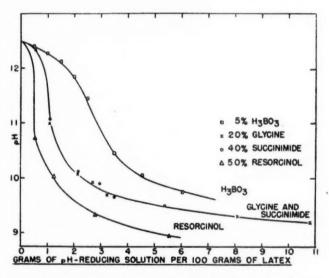
Fig. 1.—Effect of pH-reducing solutions on the pH of Neoprene latex Type 571.

soluble than resorcinol.   In some cases, however, the use of catechol may be
desirable because of its effect in accelerating the vulcanization of Neoprene[11].

Formamide has a delayed effect on the pH of Neoprene latex.   No reduc-
tion in pH is observed when formamide and latex are first mixed, but the pH
declines gradually and continually thereafter.   If as much as 1 per cent form-
amide is used, the latex coagulates within a few days (Table III).   This effect
may be due to slow hydrolysis of the formamide to give sodium formate.

Succinimide reduces the latex pH immediately, but a slow decline in pH
continues to occur during storage.   Latex that has been treated with suc-
cinimide has only a short storage life (Table III).   Resorcinol and glycine do
not cause a delayed reduction in pH; neither do they severely limit the storage
life of Neoprene latex (Table III).   As Figure 2 shows, the pH drop on aging
latex containing glycine is comparable to that for untreated latex.

TABLE III

STORAGE LIFE OF LATICES WITH REDUCED pH

Solution added	Parts active agent added to 100 parts Neoprene (200 parts Neoprene latex Type 571)	pH immediately after addition	pH after 1 day at 27° C	Days before latex coagulated in storage at 27° C
None	..	12.4	12.4	Over 170
5% glycine	0.5	11.5	11.5	Over 170
20% glycine	1.0	9.9	9.9	160
Absolute formamide	1.0	12.4	10.6	10
Absolute formamide	2.0	12.4	10.5	6
50% resorcinol	2.5	9.2	9.2	50
20% succinimide	4.0	9.5	..	1
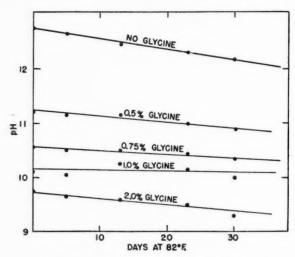
FIG. 2.—Change in pH of Neoprene latex Type 571 on aging. Per cent glycine is expressed as parts per 100 parts Neoprene.

EFFECT OF GLYCINE ON LATEX GELATION

Evaluation of the use of glycine in commercial applications showed that glycine had a pronounced effect in shortening the time between commencement and completion of gelation of latex. The gelling times of ten lots of Neoprene latex Type 60 of various ages were measured using 4 parts of sodium fluosilicate per 100 parts of Neoprene. The latex was put in a small beaker and the sodium fluosilicate added slowly with constant stirring. The time was measured from the addition of the sodium fluosilicate to the commencement of gelation (T_1) and to the completion of gelation (T_2). The pH values of the different samples of latex were measured with a Beckman pH meter using the high pH glass electrode described by Dole[12].

The effect of pH on time of gelation is illustrated in Figure 3. Not only does the gelling time (T_1 and T_2) increase with increasing pH, but the time between the start and the completion of gelling ($T_2 - T_1$) becomes much greater as the pH increases.

The ten lots of Neoprene latex Type 60 previously used in the gelation experiments were treated with sufficient glycine to reduce the pH values of all the latex samples to 9.3.   This value was chosen because the data of Figure 3 indicated that this was the highest pH at which the curves of commencement and completion of gelation remained parallel and close together.   Four parts of sodium fluosilicate were added per 100 parts of Neoprene, and the starting and finishing times of gelation were again measured.   Figure 4 compares the gelling times for the untreated latex, for which data are given in Figure 3, with the gelling times of the adjusted latex samples indicated by the cross-hatched areas of the bars.   The data show that, by adjusting the pH of the latex samples to a proper constant value, variations in both the starting and finishing times of gelation can be eliminated.
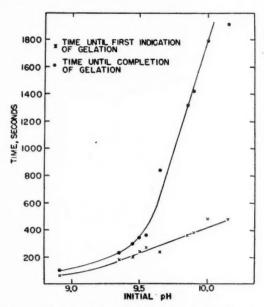
FIG. 3.—Variation of gelling time of Neoprene latex Type 60 with pH.

The actual gelling times can be varied over a wide range by varying the pH of the latex and the concentration of sodium fluosilicate.   The control of pH to any definite value can be exercised only during actual production or use of the latex mix, since the pH of Neoprene latex decreases slightly because of aging alone.

The use of glycine for pH control of latex mixes has been studied in some standard manufacturing procedures.

SPONGE MANUFACTURE

The most widely used method of manufacturing Neoprene froth sponge is to coagulate whipped compounded latex by the use of sodium fluosilicate according to the process developed by Murphy and others[14].   It is necessary that the froth remain fluid and stable for a sufficient period of time after the sodium fluosilicate has been added to allow safe transferring and pouring into the

molds. It is then desirable that gelation occur sharply. In this way uneven gel formation can be avoided.

The following formula, given in dry weight, was used in making Neoprene froth sponge:

Neoprene (from Type 60 latex)	100.0
Zinc oxide	5.0
Phenyl-β-naphthylamine	2.0
Petrolatum	5.0
Sodium dibutyldithiocarbamate	0.83
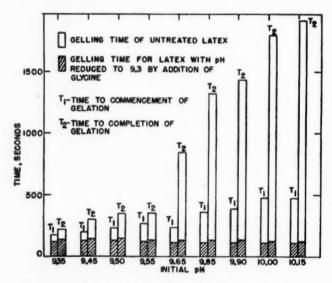
FIG. 4.—Control of gelling time of Neoprene latex Type 60 with glycine.

The latex was frothed in a Hobart mixer until the foam had reached approximately its maximum frothing height. The sodium dibutyldithiocarbamate was added as a 25 per cent solution in water. The petrolatum, phenyl-β-naphthylamine, and zinc oxide were then added as 50 per cent water dispersions. From 1 to 4 parts of sodium fluosilicate prepared as a 20 per cent ball-milled dispersion were incorporated into the froth. Whipping was continued until the sodium fluosilicate was evenly distributed throughout the foam. The froth was then poured into a lubricated mold and allowed to gel.

Sponges were prepared from several of the untreated lots of Neoprene latex Type 60. The variations in times of commencement and completion of gelation previously noted persisted in the foam sponge process and made reproducibility of gelation conditions from lot to lot impossible. The pH values of the different lots of latex were then adjusted to 9.3 with glycine. Froth sponge prepared from these adjusted lots of latex gelled sharply with little variation from lot to lot in the starting and finishing times of gelation. Glycine should be added to the froth just before the addition of the sodium fluosilicate. Approximately 20 per cent less fluosilicate is required for gelation when glycine is used.

COAGULATING DIP PROCESS

The thickness of film deposited from a compound of 10 parts of hard clay, 2 parts of phenyl-β-naphthylamine, and 5 parts of zinc oxide on 100 parts of Neoprene from Type 571 latex, using a calcium salt coagulant (1 calcium chloride, 1 $Ca(NO_3)_2.4H_2O$, 2 acetone, 6 methyl alcohol), was determined before and after the addition of 0.5 part of glycine per 100 parts of Neoprene.   Deposition rate curves (Figure 5) show that compounds prepared with glycine have a greater deposition rate than do similar compounds without this material.
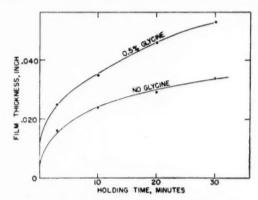
FIG. 5.—Effect of glycine on thickness of coagulating dip films.
Percentage of glycine is expressed as parts per 100 parts Neoprene.

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DESCRIPTION AND AVAILABILITY

A liquid, organic peroxide (8.00–8.50% available oxygen) which in addition to being relatively non-volatile and highly stable, is easily miscible with many Monomeric Materials, effectively catalysing these materials to form extremely clear, bubble-free films. *In limited commercial production. Samples will gladly be sent anyone interested.*

PROPERTIES

Molecular Weight	194
Available Oxygen	8.00-8.50%
Color	Light Yellow
Specific Gravity @ 20° C.	0.859
Refractive Index @ 25° C.	1.489
Vapor Pressure	Less than 10 mm. of mercury at 100° C.
Freezing Point	−2° to −4° C.
Decomposition Point	113°-116° C.
Sensitivity	Insensitive to shock, rubbing, grinding. Highly stable at room temperature.
Stability	Stable over iron, aluminum, copper, tin, zinc. Decomposes slowly over lead.
Solubility	Soluble in all proportions in all common organic solvents.

SUGGESTED USES

1. As an effective catalyst in bulk polymerizations.
2. As a good high temperature polymerization catalyst.
3. Wherever organic peroxides are of interest.

*t-BUTYL HYDROPEROXIDE

DESCRIPTION AND AVAILABILITY

An organic, alkyl peroxide that is standardized at a concentration of 60% (10.66% available oxygen). Use of proper activators increases the rate of release of oxygen. *In limited commercial production. Samples will be gladly sent anyone interested.*

PROPERTIES

Molecular Weight	90
Available Oxygen	10.66%
Color	Water White
Specific Gravity @ 25°C.	0.859
Refractive Index @ 25°C.	1.396
Boiling Range	90°-107°C.
Flash Point	18.3°C.
Freezing Point	−35°C. to −36°C.
Decomposition Temperature	76.6° C.
pH of 1 part 60% Conc. in 10 parts water	4
Solubility	60% Conc. in water 11%
	Water in 60% Conc. 5%
	In short chain aliphatics Excellent
	In aromatics Excellent

SUGGESTED USES

1. As a catalytic agent in single and two phase polymerization reactions, as for example: in the polymerization of vinyl polymers and co-polymers; in the polymerization of diene hydrocarbons used in synthetic elastomers.
2. As a source of oxygen in the drying of paints.
3. As an oxidizing agent for laboratory purposes.

*U. S. Patents 2176407, 2223807, 2298405

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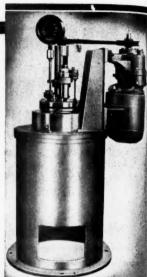
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